QUANTITATIVE CHEMICAL ANALYSIS

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LONDON: 98 GREAT RUSSELL STREET, W.C.

EDINBURGH: TWEEDDALE COURT

1942

EXTRACT FROM PREFACE TO FIRST EDITION

THIS book is intended primarily for University and College students. We have endeavoured to arrange the book in such a manner that some knowledge of the principles of Quantitative Analysis may be acquired by a practical study of the subjects included in Parts I., II., and III., and that the further requirements of those who are making a special study of Chemistry should be met by the later portions of the book.

Most of the typical exercises in Parts II. and III. may be performed with pure substances, but it is desirable that the student should be accustomed from the commencement of his course to the analysis of substances of " unknown " composition. The serious student finds that this enhances the value of the exercise, whilst the occasional student who " only wants to know the method " has his attention directed to the real purpose of Quantitative Analysis. A list of solutions suitable for analysis is given in the Appendix. In describing typical exercises, care has been taken to give the practical details of manipulation as fully as possible, and where full details are not given, reference is invariably made to the pages where they may be found.

In Part V., all the common elements and radicals are considered, together with the methods for their separation and determination. As the arrangement is alphabetical and copious references to other parts of the book are given, it is hoped that this section will prove a useful index.

In order to avoid constant repetition of particulars in regard to the concentration of reagents, it has been assumed throughout the book that, unless the contrary is stated, the concentration of a reagent is that specified in the Appendix. The concentrations usually recommended for indicator solutions are such that even

"a few drops" is often more than ought to be used. The concentrations recommended in the Appendix are so chosen that 1 c.c. of the indicator is the normal amount required, and throughout the book it is assumed that these dilute indicator solutions are used.

All the diagrams have been specially drawn for the book—in a large number of cases from original photographs of the apparatus.

CHEMISTRY DEPARTMENT
UNIVERSITY OF EDINBURGH
October 1913

PREFACE TO EIGHTH EDITION

OWING to the comparatively short time which has elapsed since the seventh edition was published, it has been considered unnecessary to make any very substantial changes in the eighth edition. Moreover, the output on analytical work suitable for a book of this kind has been considerably curtailed owing to present conditions.

The only somewhat extensive section which has been added is that on Conductometric Analysis. As in the case of the description of potentiometric titrations in previous editions, this new section has been treated in the simplest manner, and only inexpensive apparatus is required. The results which can be obtained are sufficiently accurate to illustrate the principles involved in conductometric work, the importance of which is becoming more widely appreciated.

In a review of the last edition, it was suggested that water analysis is too specialised a subject for inclusion in a textbook intended primarily for students. Whilst the revisers to some extent appreciate this point, and also realise that it is not possible in a short chapter to give a comprehensive treatment of the subject, they feel that it is advisable to leave this section in the present edition. Chemical students should be familiar with determinations such as those of hardness, and of chloride and ammonia in water. These might be given separately in the volumetric and colorimetric sections, but the chapter as it stands serves as an introduction to the subject, and should be of some value in classifying water samples if a treatise on the subject is not available.

Considerable alterations and additions have been made in Part I., and also in the introductory section of Part II., where the measurement of volumes and the standardisation of instruments is described. Much of the data for these measurements is taken from the pamphlet *Tests on Volumetric Glassware*, issued by the National Physical Laboratory, Teddington, Middlesex, and is reproduced by the courtesy of the Director.

The purification of sulphamic acid and its use as a standard in alkalimetry has been described.

As examples of comparatively new volumetric methods, the determination of barium by thiosulphate after precipitation as iodate, of iron by mercurous nitrate, of cobalt and zinc by bromate after precipitation with oxine may be mentioned. The use of standard bromate for the determination of hydroxylamine and hydrazine is also described.

A more satisfactory method for the determination of hyposulphite has replaced that described in previous editions and the determination of mercury as mercury zinc thiocyanate has been included. The determination of carbon dioxide in air has been simplified without loss of accuracy, and a colorimetric method for phosphate has been added.

For the methods given for the determination of tungsten (p. 377), molybdenum (p. 378), vanadium (p. 267), and chromium (p. 116) in steel, we are indebted to the United Steel Companies, Ltd., these being based on standard methods in use in their laboratories, and published in the revised edition of their *Standard Methods of Analysis*.

DEPARTMENT OF INORGANIC AND
PHYSICAL CHEMISTRY
UNIVERSITY OF LIVERPOOL
1942

CONTENTS

PART I.—GENERAL PRINCIPLES

PART II.—VOLUMETRIC ANALYSIS

Acidimetry and Alkalimetry

Reduction-Oxidation Processes

PART II.—VOLUMETRIC ANALYSIS—*continued*

PART III.—GRAVIMETRIC ANALYSIS

PART IV.—COLORIMETRIC METHODS

PART V.—SYSTEMATIC QUANTITATIVE ANALYSIS

PART V.—SYSTEMATIC QUANTITATIVE ANALYSIS—*continued*

PART VI.—THE ANALYSIS OF SIMPLE ORES AND ALLOYS

PART VII.—GAS ANALYSIS

PART VIII.—WATER ANALYSIS

APPENDIX

QUANTITATIVE CHEMICAL ANALYSIS

PART I

GENERAL PRINCIPLES

WHEN the examination of any substance is undertaken for the purpose of determining the respective amounts of any of its constituents, the investigation is known as **quantitative analysis.** The problem may be a simple or a complex one, depending on the nature of the substance, and on whether a complete or only a partial analysis is required. For many purposes it is not necessary to ascertain the amounts of all the constituents of a substance ; it may be of importance to determine the amount of only one of them. It is comparatively simple to determine, for example, the amount of iron in an ore, the amount of carbon dioxide in a sample of air, or the amount of chloride in a water-supply. On the other hand, it may be necessary to make a complete analysis of a complex ore or rock containing as many as ten or twenty constituents, or to carry out a detailed investigation of a sample of water. The complexity of an analysis depends, however, as much on the nature of the constituents as on their number, and the determination of the amount of even a single constituent may involve a lengthy and refined investigation, demanding the highest skill on the part of the chemist.

Different methods are usually available for the determination of one and the same constituent, but not all of those methods may be applicable to every substance containing it. The choice of the best method often requires careful consideration.

The gravimetric method of analysis usually involves (1) the separation of the constituents of the substance in the form of

insoluble compounds of known composition ; (2) the determination of the weight of the compounds so obtained.

The volumetric method of analysis, on the other hand, is based on the use of a reagent of known concentration, and on the measurement of the volume of this reagent required to complete the chemical change involved.

A fundamental distinction between the two methods is that *in gravimetric analysis* the constituent that is to be determined must be separated from all the other constituents of the substance ; whereas, *in volumetric analysis*, the separation of the constituents is very frequently unnecessary, and one or more of the constituents of a substance can often be rapidly and accurately determined in presence of all the others, thus enormously simplifying the analytical process.

Most substances can be determined either gravimetrically or volumetrically. In the systematic treatment of the subject it is convenient to consider gravimetric and volumetric methods separately ; but in practice the two methods of procedure are frequently combined, in order that the analysis may be completed as rapidly and as accurately as possible. When a complete analysis of a complex substance has to be made, the constituents must, as a rule, be separated from one another before the amount of each can be ascertained, and gravimetric methods are usually employed ; whereas, if only a partial analysis is required, involving, it may be, only one of the constituents, volumetric methods are often applicable. The latter are almost invariably more expeditious than gravimetric methods, and in analysis for technical purposes where economy of time is often imperative, volumetric methods—not necessarily less accurate than gravimetric—are used as far as possible.

As an example in illustration of some of the foregoing principles, two methods of determining the respective amounts of iron and aluminium in a solution containing ferric and aluminium chlorides may be briefly outlined.

(1) In order to accomplish this by gravimetric methods alone, *the iron and aluminium must be separated* by adding an excess of sodium hydroxide to a weighed or measured portion of the solution. The *precipitate*, which consists of ferric hydroxide, is filtered ; the *filtrate* contains the aluminium as sodium aluminate.

The *precipitate*, which is contaminated with alkali hydroxide,

is dissolved in dilute acid, and ammonia is added in order to reprecipitate the ferric hydroxide. The latter, after filtration, is converted into ferric oxide which is weighed.

The *filtrate*, containing the sodium aluminate, is acidified with hydrochloric acid, and the aluminium is precipitated as aluminium hydroxide by adding ammonia. The precipitate is filtered and, by heating to a high temperature, is converted into alumina which is weighed.

From the weights of ferric oxide and alumina, the respective amounts of iron and aluminium in the solution can then be calculated.

(2) By a combination of gravimetric and volumetric methods, which in this case is much to be preferred, *no separation of the iron and aluminium is necessary*; the procedure is accordingly simpler and more expeditious, and accurate results are more readily obtained.

The iron and aluminium are precipitated together as hydroxides by adding ammonium chloride and ammonia to a weighed or measured portion of the solution, and the precipitate, by heating strongly, is converted into a mixture of ferric oxide and alumina which is weighed. The mixture of ferric oxide and alumina is then dissolved (or another measured portion of the original solution is taken), and the iron in the solution is determined volumetrically. The volumetric process consists, briefly, in reducing the ferric salt to the ferrous state by means of some suitable reducing agent, and in then determining the amount of iron present by means of a solution of potassium permanganate of known concentration. The aluminium does not interfere with the volumetric determination of the iron.

It is then easy to calculate how much ferric oxide is present in the mixture of ferric oxide and alumina, and the difference between the total weight of the mixed oxides (which has already been determined gravimetrically) and the weight of the ferric oxide is the weight of the alumina. The respective amounts of iron and aluminium in the original solution can then be calculated.

The Balance

For accurate analytical work, a suitable balance, capable of supporting a maximum load of 100 to 200 grams in each pan, is indispensable. It is important that the maximum load, whatever it may be, should never be exceeded. With a good balance, properly adjusted and used, very accurate measurements can be made. For example, it is possible to distinguish between two masses of about 10 grams each when they differ in weight by only 0·1 milligram, *i.e.* by 1 part in 100,000. A balance is, therefore, a delicate instrument of precision, and the greatest possible care must be taken in using it. *The rules regarding the use of the balance* (p. 11) *must be carefully read and thereafter strictly adhered to.*

When weighing in a comparatively rough fashion, it is generally assumed that equipoise is established when the excursions of the pointer towards either side of the mid-point of the scale are of equal amplitude. For the following reasons, however, this method is not invariably adopted in accurate work.

(1) The zero-point, or resting-point of the unloaded balance, *i.e.* the position which the pointer would apparently take up if the oscillating beam were allowed to come to rest, seldom coincides exactly with the mid-point of the scale.

(2) Since the oscillating beam, if left to itself, ultimately comes to rest, the amplitude of each oscillation, even when equipoise is established, is *less* than that of the preceding one. It follows that, if an excursion of the pointer to the left is equal to the preceding one to the right, the weight on the right is greater than that on the left (assuming the zero-point to coincide with the mid-point of the scale).

Routine Method of Weighing

In making a weighing, accurate to 0·1 milligram (0·0001 gram), the following method should be used :—

(1) Find the *zero-point* of the balance.

Release the beam carefully, and if necessary set it oscillating so that the pointer moves through about five scale divisions on

either side of the middle point. If it does not oscillate sufficiently, on releasing the beam, this may be brought about by gently opening the balance-case, and wafting air down on to one of the pans and closing the case again. A more satisfactory method is to fit a glass tube through the left-hand side of the balance-case, with one end slightly turned up under the left pan. A rubber bulb is connected to the other end of the tube outside the balance-case. A slight puff of air is sufficient to start the beam swinging, and to increase or decrease the amplitude. Neglecting the first complete oscillation (two excursions of the pointer), carefully observe and note down the next *three* extreme positions of the pointer, two observations being made on one side and one on the other side of the mid-point of the scale. Assume the scale to be numbered from the extreme left towards the right, *e.g.* from 0 to 20, the mid-point being 10, and estimate tenths of the scale divisions.

If, for example, the observations were

Left.	Right.
(1) 5·0	
	(2) 15·8
(3) 5·4	

the turning-point on the left, corresponding to the point 15·8 on the right, is the mean of 5·0 and 5·4, *i.e.* 5·2, and the resting-point is therefore

$$\frac{5{\cdot}2+15{\cdot}8}{2} = 10{\cdot}5$$

Repeat the observations several times. The results should not differ by more than one or two tenths of a scale division, and the mean is taken as the zero-point of the balance. As the zero-point is frequently subject to slight fluctuations, it should be determined before each set of weighings is commenced.

(2) Place the vessel to be weighed on the *left* pan of the balance and proceed to counterpoise it. It is best to begin with a weight that will probably prove too heavy, as this may save time in the end. For example, if the weight of the vessel is thought to lie between 15 and 20 grams, the latter weight is placed on the right scale-pan. If, on releasing the beam, the 20-gram weight is seen to be too much, it is replaced by a

10-gram weight, and the necessary smaller weights are added *in regular succession* until the sum of the weights on the right-hand pan is within 0·01 gram less than the weight of the object: *e.g.* if 16·46 grams is too little and 16·47 grams is too much, the smaller weight is left on the pan.

In place of the inconveniently small milligram weights, it is preferable, at this stage, to use a rider, which weighs 0·01 gram, though its effective weight depends on its position on the divided beam. After some experience it will be found possible approximately to estimate, by observing the rapidity of the movement, what additional weight is required to establish equilibrium. If, for instance, it has been found that with 16·46 grams on the pan the pointer is deflected slowly to the right whilst with 16·47 grams it is deflected much more rapidly to the left, the weight of the vessel is nearer 16·46 than 16·47 grams.

Now close the balance-case, and place the rider on the beam in such a position that equipoise is nearly established—for example, at division 3. The beam should be arrested before changing the position of the rider, though after some experience slight alterations may be made while the beam is swinging. Record three oscillations of the pointer, and determine the resting-point. Suppose it is found to be 9·6.

(3) Find the "sensitiveness" of the balance, *i.e.* the displacement of the resting-point produced by an alteration of 1 milligram:—Alter the position of the rider by an amount corresponding to 1 milligram—in such a direction that the resting-point is shifted to the other side of the zero-point—and again determine the resting-point. Suppose it to be 11·1 when the rider is at division 2. The sensitiveness is then equal to

$$11{\cdot}1 - 9{\cdot}6 = 1{\cdot}5 \text{ scale divisions.}$$

(4) Now calculate, as follows, the alteration of the weight necessary to counterpoise the vessel exactly:—

The zero-point—using the figures assumed in the foregoing—is 10·5, and the resting-point with a load of 16·462 grams is 11·1. The vessel weighs, therefore, more than 16·462 grams, the additional amount being equal to that necessary to displace the resting-point from 11·1 to 10·5, or 0·6 of a scale division. Since, however, 1·5 scale divisions correspond to

1 milligram, 0·6 scale division is equivalent to

$$\frac{0{\cdot}6}{1{\cdot}5} = 0{\cdot}4 \text{ milligram.}$$

The weight of the vessel is therefore 16·4624 grams.

The complete weighing thus involves the determination of three resting-points—the first, that observed with the empty balance; the second, after approximately counterpoising; the third, after making an alteration of ± 1 milligram. All the observations made in the above example are shown below:—

Resting-points

	(1) Unloaded balance.		(2) With load of 16·463 grams.		(3) With load of 16·462 grams.	
	5·0		4·4		6·7	
		15·8		14·7		15·3
	5·4		4·6		7·0	
Mean	5·2	15·8	4·5	14·7	6·9	15·3
Resting-points	10·5		9·6		11·1	

Sensitiveness = 11·1 − 9·6 = 1·5 scale divisions
Deviation = 11·1 − 10·5 = 0·6 ,, ,,

Additional weight $= \frac{0{\cdot}6}{1{\cdot}5} = 0{\cdot}4$ milligram

Weight of vessel = 16·462 + 0·4 milligram
= 16·4624

Determination of the Sensitiveness of the Balance with Different Loads

It is evident from the foregoing that the process of weighing may be considerably shortened if the sensitiveness of the balance is already known. The sensitiveness usually varies with the load, and may either increase or decrease with the load, according to the construction of the balance. Good modern balances are so constructed that the sensitiveness is practically constant for all loads up to the limit for which they are intended to be used.

Determine, then, the sensitiveness with 5, 10, 20, and 50 grams in each pan. There is some advantage in placing an excess of 5 mg. on the left scale-pan in order that equipoise may be established with the rider near the middle of the right arm of the balance. The resting-point is then determined with the rider in two positions, differing by 1 or by 2 milligrams,

and so chosen that the resting-points are found on opposite sides of the zero-point. From the observations calculate the sensitiveness with each load, that is, the displacement of the resting-point produced by an alteration of $\pm$ 1 milligram, and keep a record of the results in a note-book.

Having determined the sensitiveness in this way, once for all, the process of weighing resolves itself into the following two operations :—

(1) Find the zero-point of the balance.
(2) Counterpoise the object to the nearest milligram and find the resting-point.

The fraction of a milligram that must be added (or subtracted) to complete the counterpoise is then calculated. If, for example, the zero-point is 10·2, the resting-point 9·7 with a weight of 5·826, and the sensitiveness 1·7, then the correct weight is $\frac{10\cdot2-9\cdot7}{1\cdot7}=\frac{0\cdot5}{1\cdot7}=0\cdot3$ milligram less than the weight on the balance-pan ; that is, 5·8257 grams.

Abbreviated Method of Weighing

It is often permissible, in practice, to shorten the routine method of weighing and thus to save time, without sacrificing the necessary accuracy. The abbreviated procedure varies with the circumstances, as follows :—

(1) When the required weight is to be ascertained by "difference," *e.g.* the difference between (*a*) the weight of an empty vessel, and (*b*) the weight of the vessel and substance, *and when the two weighings involved are consecutive*, the zero-point of the balance may be assumed to be 10 for both weighings. The same error (if any) will appear in both weighings, but the difference will give the accurate weight of the substance.
(2) When more than 1 gram of substance is to be weighed, the position of the rider may be adjusted by trial until the excursions of the pointer on either side of the mid-point of the scale are of equal amplitude or nearly so, allowing for the gradual decrease in extent

of swing. A preliminary trial will make it possible to estimate by how much the rider must be moved to correct a given inequality in swing. The error involved need not exceed 0·5 milligram, or 0·05 per cent. if the substance weighs 1 gram. This error is usually negligible in comparison with other experimental errors (*cf.* p. 23).

Sources of Error in Weighing

The following factors must be taken into consideration in accurate weighing :—

(1) The effect of inequality in the length of the right- and left-hand arms of the balance.
(2) The effect of buoyancy of the air on the object and weights.
(3) A possible change in the weight of the containing vessel between successive weighings.
(4) A possible change in weight of the substance being weighed.
(5) Errors in the value of the weights themselves.

These errors may be eliminated as follows :—

(1) The error due to unequal lengths of balance-arms is proportional to the load, and in weighing small objects can usually be neglected, when using a good balance. Also, the error will be nearly eliminated when weighing a vessel empty and then with a gram or so of material, provided the vessel is always placed on the same pan of the balance. The error can be completely eliminated by the tare method, or by the method of double weighing. In the former, the object is counterpoised by a spare set of weights which need not be accurate ; accurate weights are then substituted for the object. In the latter method, the object is first put on the left-hand pan, and the apparent weight W_1 is obtained with accurate weights on the right-hand pan. The object and weights are then interchanged, and the apparent weight W_2 found with the accurate weights on the left-hand pan. If x equals the true weight of the object, and R and L are the lengths of the right-hand and left-hand arms respectively, then

$$xL = W_1R, \text{ and } xR = W_2L.$$

By multiplying these equations together, and eliminating RL from both sides, we obtain

$$x^2 = W_1W_2, \text{ or } x = \sqrt{W_1W_2}$$

Since in practice W_1 and W_2 are very nearly equal, x may be taken as $\frac{W_1+W_2}{2}$.

(2) The buoyancy of air introduces a considerable error if the density of the object being weighed differs greatly from that of the weights, though, unless great accuracy is necessary, the error due to this cause may be neglected in the case of a solid whose weight is not more than 0·5 gram. No further error is, of course, introduced by the volume of the container which is weighed with and without the solid. It is, however, essential to correct for the air displaced when weighing considerable volumes of a material of low density, and especially in weighing vessels containing gases. The true weight, *i.e.* the weight *in vacuo*, is given by the following formula to a very close approximation :—

$$W_x = W_a + W_a \times D_a\left(\frac{1}{D_s} - \frac{1}{D_w}\right)$$

where W_x is the true weight, W_a the weight in air, D_s the density of the substance being weighed, D_w the density of the weights used, and D_a the density of air (*i.e.* the weight of 1 millilitre (see p. 484)) under the conditions of temperature, pressure, and humidity obtaining, usually about 0·0012 gram.

(3) The weight of the containing vessel may have changed by absorption or loss of moisture, and it may also show an apparent change in weight due to electrification of the surface or to its temperature being different from that of the balance-case.

These sources of error may be largely eliminated by wiping the vessel gently with a linen cloth, and allowing it to stand twenty minutes or more in the balance-room before weighing. The electrification produced by rubbing is largely dissipated after this interval of time.

If the container is weighed at first when filled with air, it is advisable to make subsequent weighings when it is again filled with air, unless a correction can be calculated to allow for the presence of a gas of different density.

(4) Hygroscopic, efflorescent, and volatile substances should,

of course, be weighed in closed vessels, and it should be remembered that finely divided dry powders will rapidly pick up moisture in the air.

Rules to be Observed in Using the Balance

It should be remembered that one incorrect weighing spoils the whole analysis.

(1) The object to be weighed must be at room temperature. If it has been heated, sufficient time must be allowed for cooling. The time required to attain the room temperature varies with the size, etc., of the object, but as a rule twenty minutes is sufficient.

(2) Glass vessels, after handling, should be wiped with a linen cloth, and then left in the balance-room for at least twenty minutes before weighing. This is necessary more especially in the case of large vessels, such as flasks, U-tubes, etc., the weight of which may vary by several milligrams according to the conditions under which they are weighed.

(3) Never place a chemical to be weighed directly on the balance-pan, but place it on a watch-glass or scoop, or in a weighing-bottle. When it is necessary to add more of a solid or liquid, the operation must be performed outside the balance-case.

(4) Liquids and volatile solids must be weighed in a closed vessel, such as a stoppered weighing-bottle. If the vapour is corrosive, the vessel should not be opened in the balance-room.

(5) Sit opposite the middle point of the balance.

(6) Release the beam (and arrest it) gently, and, if necessary, set it swinging by a draught of air (see p. 5). The pans must not swing from side to side.

(7) Find the zero-point of the balance before each set of weighings.

(8) The pointer should move through four or five divisions beyond the mid-point of the scale. The pans must on no account be touched while the beam is swinging.

(9) Lift the weights with the forceps only.

(10) Before placing anything on the balance-pan, or removing anything therefrom, the balance must be arrested.

(11) Always close the balance-case when starting to use the rider.
(12) Note the weight in a note-book (not on a loose slip of paper which is apt to be lost) *before* removing the weights from the pan by noting the empty places in the box, and check the weights as they are being removed from the pan. Remove the rider from the beam.
(13) Never leave anything on the pans when weighing is finished. Any chemical spilt in the balance-case must be removed at once.
(14) Close the balance-case when finished.

Exercises in Weighing

Read the description given of the routine method of weighing (pp. 4 to 8) and, after careful study of the rules to be observed in using the balance, proceed to practise the following exercises, in order to become familiar with the balance and the method of using it. Make notes of your observations and submit them for inspection.

(1) Find the zero-point of the balance. Repeat the operation four times (at least), arresting the balance after each. Keep a record of your observations as shown on p. 7.
(2) Find the sensitiveness of the balance with loads of (*a*) 5 grams, (*b*) 10 grams, (*c*) 20 grams, (*d*) 50 grams in each pan.
Tabulate the results and draw a graph showing the variation of sensitiveness with the load.
(3) Clean a porcelain crucible and lid. Weigh to 0·1 milligram, (*a*) the crucible, (*b*) the lid, (*c*) the crucible and lid. Keep a record of all the observations from which the zero-point, the various resting-points, and the final results are obtained.

Calibration of Weights

Reference has been made above to possible errors introduced by the weights themselves. Since in most cases only *weight ratios* and not *absolute weights* are of importance in analytical

chemistry, it is not essential that the unit weight adopted should represent a true or standard gram; but it is imperative that the various pieces in a set should agree amongst themselves, *e.g.* that each of the 1-gram weights should be exactly 100 times the weight of each centigram, and one-tenth that of each 10-gram piece. It ought to be an invariable rule to test a set of weights before it is used for accurate work.

The brass weights in a set usually comprise the following pieces:—

$$50, \quad 20, \quad 10', \quad 10'', \quad 5, \quad 2, \quad 1', \quad 1'', \quad 1'''.$$

The weights of the same nominal value are usually provided with distinguishing marks; if there are none, one or more *minute* marks must be made upon them with the point of a knife before beginning the calibration. The comparison of the weights is made by the method of "double weighing" (see p. 9). The procedure is as follows:—

Find the zero-point of the balance. Place the 50-gram weight on the left scale-pan and the remainder of the brass weights on the right. Determine the resting-point. If it differs from the zero-point, find, by the method already described, what additional weight must be added to either side of the balance in order to give exact counterpoise. Now interchange the weights, placing the 50-gram weight on the right, and again determine the difference between the loads. If, for example, the two weighings were

Left. Right.

$$50+2{\cdot}0 \text{ mg.} = 20+10'+10''+5+2+1'+1''+1''',$$

and $$20+10'+10''+5+2+1'+1''+1''' = 50+0{\cdot}4 \text{ mg.},$$

the average of the two weighings is

$$50+1{\cdot}2 \text{ mg.} = 20+10'+10''+5+2+1'+1''+1''',$$

or $$50 = 20+10'+10''+5+2+1'+1''+1'''-1{\cdot}2 \text{ mg.}$$

In the same way, compare the 20-gram weight with the sum of 10′ and 10″, 10′ with 10″, and 10′ with the sum of 5, 2, 1′, 1″, and 1‴.

As the effect of inequality of the arms varies with the load, if it is found at this stage with 10 grams in each pan that the difference between two weighings is not more than 0·2 milligram, only one weighing need be made in comparing the smaller weights. Proceed then, further, to compare the 5-gram weight

with the sum of 2, 1′, 1″, and 1‴; the 2-gram weight with 1′+1″, and also 1″ with 1′, and 1‴ with 1

In the first and second columns of the following table the results obtained with a set of weights are arranged in order, beginning with the small weights.

Nominal value of weights.	Observed results of double weighings.		Calculated value of each piece in terms of weight marked 1′.
		mg.	mg.
1′	= provisional unit.		= 1′
1″	= 1′	−0·1	= 1′−0·1
1‴	= 1′	+0·1	= 1′+0·1
2	= 1′+1″	±0	= 2×1′−0·1
5	= 2+1′+1″+1‴	−0·2	= 5×1′−0·3
10′	= 5+2+1′+1″+1‴	−0·5	= 10×1′−0·9
10″	= 10′	−0·2	= 10×1′−1·1
20	= 10′+10″	−0·5	= 20×1′−2·5
50	= 20+10′+10″+5+2+1′+1″+1‴	−1·2	= 50×1′−6·1
Total 100	= 50+20+10′+10″+5+2+1′+1″+1‴		= 100×1′−11·0

Now select, as a provisional unit, one of the single gram pieces, say 1′, and express the value of each of the others in terms of this unit. The result of this is shown in column 3. The transformation is easily made if the successive rows are extended in order, beginning with the first. For instance, the 5-gram weight is equal (see column 2) to the sum of the preceding weights minus 0·2 milligram; but (column 3) the sum of the preceding weights is equal to 5×1′−0·1 milligram, therefore the 5-gram weight is equal to 5×1′−0·3 milligram.

The choice of a small weight as the unit of comparison throws a big error on the larger weights. In order to secure a uniform distribution of the relative errors, the assumption is now made that the sum of all the weights is exactly 100 grams, and the value of the provisional unit, on this assumption, is calculated.

The sum of the weights,

100×1′ − 11·0 milligrams = 100 grams,

or 100×1′ = 100 grams+11·0 milligrams,

or 1′ = 1 gram+0·11 milligram.

The value of the provisional unit, 1′, is thus 1 gram+0·11 milligram.

Now substitute this value for each 1′ in column 3 of the table on p. 14. The following are the results :—

Nominal value.	Actual value.		Error.
1′	= 1 gram + 0·11 mg.	= 1·0001	+ 0·1 mg.
1″	= 1 gram + 0·11 mg. − 0·1 mg.	= 1·0000	*nil.*
1‴	= 1 gram + 0·11 mg. + 0·1 mg.	= 1·0002	+ 0·2 mg.
2	= 2 grams + 0·22 mg. − 0·1 mg.	= 2·0001	+ 0·1 mg.
5	= 5 grams + 0·55 mg. − 0·3 mg.	= 5·0003	+ 0·3 mg.
10′	= 10 grams + 1·1 mg. − 0·9 mg.	= 10·0002	+ 0·2 mg.
10″	= 10 grams + 1·1 mg. − 1·1 mg.	= 10·0000	*nil.*
20	= 20 grams + 2·2 mg. − 2·5 mg.	= 19·9997	− 0·3 mg.
50	= 50 grams + 5·5 mg. − 6·1 mg.	= 49·9994	− 0·6 mg.
Total 100		= 100 gms.	+ 0·0 mg.

It will be observed that the sum of all the errors is now zero, a necessary consequence of the assumption that the sum of all the weights is equal to 100 grams. The error in the 50-gram piece is now −0·6 milligram, and the minus sign indicates that, when the 50-gram weight is used in a weighing, 0·6 milligram should be *deducted* from the observed weight. It may be noted, however, that in a " difference " weighing, if the same pieces as far as possible are used, the actual error in the result may be nil, or very small, even if the corrections are not applied.

The sum of all the fractions, viz., ·5+·2+·1′+·1″+·05 +·02+·01′+·01″+·01‴ (the rider), is next compared with one of the single gram weights. Finally, the fractions themselves are compared with one another and, if more than negligible differences are found, the errors in the individual fractions are computed in the manner already indicated.

It is convenient to construct a table showing the amount to be added or subtracted when using any combination of weights. Four columns are necessary, showing the corrections, (1) when using 10, 20, . . . 90 grams ; (2) when using 1, 2, . . . 9 grams ; (3) when using ·1, ·2, . . . ·9 grams ; and (4) when using ·01, ·02, . . . ·09 grams.

Modern Balances

Some modern balances are fitted with a device whereby the use of a rider is dispensed with, and weighings may be made more rapidly. A light chain is attached at one end to the

balance beam, and at the other to a hook affixed to a block which slides up and down a graduated vertical column, the movement being controlled from outside the balance-case. According to the position of the block, a greater or smaller proportion of the weight of the chain is carried by the balance beam. The vertical column is so graduated that milligrams and tenths of a milligram can be read off directly from the position of the block, a vernier scale being provided. Some balances have a device which damps the swing to such an extent that the pointer comes to rest at the end of the first swing after releasing the beam; and in some balances the milligrams to be added to or subtracted from the weights in the pan can be read directly from the resting position of the pointer.

NOTES ON GENERAL APPARATUS

The following notes are intended to form a guide in the selection of suitable sizes and shapes of certain common pieces of apparatus. The special apparatus required for volumetric and for gravimetric analysis is described in Parts II. and III. respectively.

Wash-bottle.—A 500 to 700 ml. round flask (Fig. 15, p. 31) is the most convenient size. The jet, which must deliver a fine stream of water, should be within easy reach of the forefinger, in order that only one hand may be necessary to manipulate the wash-bottle (Fig. 16, p. 31). Thick string should be wrapped round the neck of the flask in order to protect the hand when hot water is used.

Beakers.—The most satisfactory beakers for quantitative analysis are made from special resistance glass (*e.g.* Pyrex glass) and are provided with a spout. The spout is not only for convenience in pouring, but it forms an outlet for steam or escaping gas when the beaker is covered with a clock-glass; it prevents the sealing of the beaker with a ring of liquid, portions of which may be projected and lost during boiling. The spout also forms a convenient place at which a stirring-rod may protrude from a covered beaker (Fig. 8, p. 27).

The size of a vessel must be chosen with due regard to the total volume of liquid which it is to contain, *i.e.* neither too large nor too small: for precipitations in gravimetric analysis,

300 ml. and 400 ml. beakers (12 to 14 cm. high) are the most generally useful sizes, and for ordinary titrations 200 ml. and 300 ml. *conical* beakers (Fig. 1).

Flasks.—Conical flasks (200 to 400 ml.) with wide mouths (2·5 cm.) are convenient for many purposes.

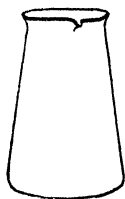



FIG. 1. FIG. 2.

Casseroles.—Porcelain casseroles (Fig. 2) are used for the same purposes as porcelain basins, and are more convenient to handle.

Funnels.—The most useful sizes are about 5·5 cm. and 7 cm. in diameter. The sides of funnels must be plain, and should enclose an angle of 60°. The stem should be not less than 8 cm. long and about 4 mm. in diameter (internal). Funnels with short, wide stems are unsuitable for filtration purposes. Some funnels filter rapidly and others slowly, and the variation in this respect is very marked. It is worth while testing a number of funnels and selecting the best.

Stirring-rods.—Very light rods for use in beakers may be made from glass *tubing*, 4 to 5 mm. in diameter, by carefully sealing *both* ends in the blowpipe flame. Open glass tubes must not be used as stirring-rods. If made from glass rod, the ends should be rounded in the Bunsen or blowpipe flame. A stirring-rod should be suitable in length for the size and type of the vessel in which it is to be used, *e.g.* 2 cm., at most, longer than the diameter of a basin, or about 5 cm. longer than the height of a beaker (Fig. 8, p. 27). If the beaker has no spout and is to be covered with a clock-glass without removing the rod, a shorter rod is required—one that will rest obliquely inside the beaker without touching the clock-glass. Rubber-tipped rods are used for a special purpose only (see p. 35) and should not be used for stirring solutions.

Boiling-rods.—In order to prevent a boiling liquid from

superheating and "bumping," a boiling-rod may be used. A boiling-rod is made from a piece of glass tubing which is closed at one end, and sealed *near* the other end, as shown in Fig. 3. The open end must be cut off so as to leave a little cup about 0·5 cm. deep, and this end is immersed in the liquid. When the rod is removed, the liquid in the cup-shaped end must be shaken out and the rod rinsed with a jet of water.

FIG. 3.

Desiccators.—A desiccator is used (1) to keep hygroscopic substances dry or (2) to effect the actual drying of wet substances. Dehydration in an ordinary desiccator is a comparatively slow process and requires many hours or even days. An evacuated desiccator is more efficient.

Either concentrated sulphuric acid or lumps of fused calcium chloride may be used as the drying agent. The layer of sulphuric acid should not be more than 0·5 cm. deep, and if the desiccator is in regular use the acid should be renewed occasionally. The ground rim of the desiccator should be greased with vaseline, sparingly used.

When extreme drying conditions are required, phosphorus pentoxide is used. It is advisable to place this in a small dish inside the desiccator to prevent the possibility of cracking when the partially exhausted phosphorus pentoxide is washed out. An efficient drying agent recently introduced is magnesium perchlorate, used either as the trihydrate or as the anhydrous salt, the latter being known as "anhydrone."

Wire Gauze.—Tinned iron wire gauze, 12·5 cm. square with an asbestos centre, is very durable, and forms a satisfactory and flat support for a beaker or flask that is to be heated.

Paper Mats.—By placing beakers and flasks containing liquid, not directly on the bench top, but on paper mats (10 cm. in diameter) or on pieces of thick blotting-paper, the risk of scratching the glass with sand grains, etc., often the cause of subsequent fracture, is avoided.

PREPARATION OF THE SUBSTANCE FOR ANALYSIS

Pure Salts.—The salts of commerce described as analytical reagent are of a definite standard of purity and may be used without special purification, as a rule, for practising typical methods of analysis and for the preparation of standard solutions.

In the case of a salt of doubtful purity, a good specimen can usually be obtained by recrystallisation. Twenty grams or more of the salt are dissolved in the minimum quantity of hot water contained in a beaker. The hot solution is poured through a fluted filter placed in a funnel with a very short stem (1 to 2 cm.), and the clear filtrate is received, with constant stirring, in a porcelain basin which is cooled by placing it in a large dish containing cold water. If much crystallisation is liable to occur during filtration, this may be carried out in a filter funnel heated by steam or electrical means. Alternatively, the filtration of the hot saturated solution may be effected rapidly by suction through a Büchner funnel (Fig. 4), in which a circle of filter paper is placed to cover the perforations. The filtrate is collected in a previously heated filter-flask (Fig. 18, p. 36), and then rapidly poured into a conical flask, which can be cooled in a stream of water while the flask is shaken.

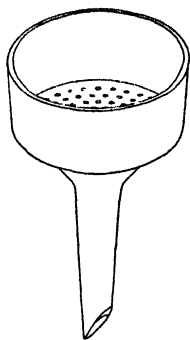



Fig. 4.

The fine crystalline " meal " thus obtained is purer than a product consisting of large crystals formed during slow cooling, as these may enclose some of the mother-liquor. The fine crystals are then separated from the mother-liquor by filtration through a Büchner funnel. The salt is well pressed down in the funnel and the mother-liquor removed as far as possible by means of the filter-pump, washing with a little cold water unless the salt is very soluble. The crystals are pressed between filter paper and then " air-dried " for twelve hours, first by spreading upon filter paper, and then, as paper is itself hygroscopic, on a clock-glass, dust being excluded. Salts which effloresce must be dried as quickly as possible and bottled. Deliquescent salts require special treatment. If the salt contains no water of hydration, it may be dried in a vacuum

desiccator; and if it suffers no alteration at 100° or at higher temperatures, it may be dried in the steam-oven or air-oven.

Metals and Alloys.—In the case of the softer metals, pieces suitable for analysis may be cut from the main sample by means of shears, or the metal may be rolled, in a steel rolling-press, into thin ribbon or foil. If this is not practicable, a representative sample should be obtained in the form of borings (by means of a steel drill), which should be taken from a number of different parts, as segregation may have taken place on solidification. If the borings are contaminated with oil, they must be washed with ether and then dried.

Mineral, Rocks, and Ores

Sampling.—In the first place, a sample suitable for analysis must be obtained. If the material is more or less homogeneous, sampling is comparatively simple, since a small, picked sample will usually be representative of the whole; whereas, if the material is a bulky, heterogeneous mass, such as a consignment of ore or coal, it is by no means an easy matter to obtain a sample that will represent as far as possible the average composition.

Procedure when an Average Sample is required.—The sampling of ores and other commercial products is a matter of great importance, since their market value is based on the results of the analyses of small samples. Full details of the elaborate methods that are often found necessary in commercial practice cannot be given here, but a general outline of the procedure is as follows:—

(1) A *large* representative sample is obtained. Any "selection" of pieces different from the average in quality is avoided by taking portions according to some rigid system; for example, a shovelful is taken from each barrow-load or truck-load.

(2) The large sample is then ground to a coarse powder and thoroughly mixed, and portions of this are again taken systematically, and the process of reduction in size and quantity repeated until a sample small enough to be sent for analysis is obtained.

The sample received by the analyst would be treated on the following lines:—

Small representative portions for analysis are obtained by spreading the sample on a piece of oil-cloth or tough paper 75 cm. square, and mixing further by lifting and pulling each corner in turn towards the opposite corner. The particles roll over each other, and the lower layers are brought uppermost. The mass is then shaped into the form of a flattened cone, and divided through the centre by two vertical cuts at right angles to each other. Two opposite quarters are rejected, and the remaining quarters are further ground, remixed on the cloth, and again quartered. This process is repeated until finally a sample is obtained, the size of which depends upon the type of analysis required. Even this sample should not be taken as absolutely homogeneous, and therefore in weighing small quantities, portions should be selected from several different parts of the sample.

Procedure when a Picked Sample is required.—If the substance is a mineral, a clean sample as free as possible from adhering gangue should be " selected." By roughly crushing the mineral, it is often possible to detach any material foreign to the mineral proper. In the case of rocks, a few chips broken from a hand specimen will usually be representative. The picked sample, which should weigh about 10 grams, must be powdered.

Crushing and Grinding.—If the material is hard, it is first broken into coarse powder on a hard steel plate (about 10 cm. square and 4 cm. thick) with a hardened hammer. Loss of flying fragments is prevented by means of a steel ring (8 cm. in diameter and 2½ cm. high) which is laid on the steel plate, or in some other manner.

A " percussion " mortar (Fig. 5) may be used for crushing small lumps. The mortar consists of three pieces—a block (A), a hollow cylinder (B), and a pestle (C)—all of very hard steel. The selected lumps, one piece at a time, are placed in the cylinder (which fits into a depression in the block) and are crushed by striking the pestle with a hammer.

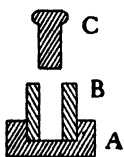



FIG. 5.

The coarsely powdered substance is then ground in an agate mortar *in very small quantities at a time.*

In order that the decomposition of the mineral by acids or

by fusion with alkali carbonates, etc., may be successfully accomplished, a very fine powder is often essential; on the other hand, prolonged powdering is not always necessary and may even lead to error in the analysis. If the mineral contains ferrous compounds, for example, partial oxidation of the iron may occur during the grinding process. Finely ground powders may also take up an appreciable amount of water from the air, and water of hydration may be expelled from minerals by long-continued grinding. Each mineral or rock demands individual treatment in this respect and it is impossible to give general rules.

WEIGHING THE SUBSTANCE

The accuracy required in this operation depends on the amount of substance that is to be weighed. If less than 1 gram is to be taken, all weighings ought to be accurate to 0·1 milli-

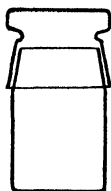



Fig. 6.

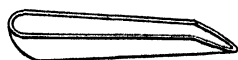



Fig. 7.—Scoop for Weighing.

gram. If several grams are necessary, weigh to the nearest milligram; and if the amount is, say, 10 grams, weigh to the nearest centigram. The weight of the substance is always found by "difference," and is usually determined in one of the following ways:—

(1) Place 3 to 4 grams of the substance, or a larger quantity if necessary, in a clean, dry weighing-bottle (Fig. 6), and weigh the bottle and its contents. Shake from the bottle (into the vessel in which the next operation is to take place) a quantity that, judged by the eye, is approximately equal to the amount prescribed, taking care that none of the substance is lost in the process. Weigh the bottle with the remaining substance again. The difference between the two weighings gives the weight of substance taken.

It does not matter if the weight is a little more, or a little less, than that desired. If it is considerably less, a further quantity may be shaken out and the second weighing repeated. If it is considerably more, no attempt should be made to return part of the substance to the weighing-bottle, but the whole operation should be commenced afresh. The bottle should be handled as little as possible between the weighings.

(2) Weigh a glass scoop. (A watch-glass may be used instead.) With the forceps lift the scoop off the balance-pan, and, with a spatula, place upon it what is judged to be the right quantity of the substance. Reweigh the vessel and contents. (It saves time in subsequent weighings if the weight of the empty vessel is marked upon it by means of a writing diamond.)

(3) If the vessel in which the substance is to be dissolved, heated, etc., is comparatively small and light, such as a crucible, weigh the substance directly in the tared vessel.

The first method should be used if several portions of the substance have to be weighed, the separate quantities being successively shaken out of the weighing-bottle which is weighed after each operation.

Liquids and volatile or hygroscopic solids *must* be weighed in a stoppered weighing-bottle.

Vessels that are to be weighed should not be placed directly on the working-bench but on a sheet of clean paper.

ERROR IN QUANTITATIVE WORK

All quantitative determinations are liable to error, however carefully carried out, and at best they only approximate to the true value of the quantity sought. In considering experimental error, a distinction should be drawn between precision and accuracy. When analytical work is carried out with a high degree of precision, the results obtained in a series of determinations of any constituent agree closely amongst themselves. It does not however follow that they approximate to

the true value, as some constant error may be affecting all the determinations. On the other hand when the work has been carried out with a high degree of accuracy, the results will be closely grouped round the true value, some below and some above. By taking the mean of such determinations a close approach to the true value will be attained.

Errors are of two kinds : (1) Those which are unavoidable. A series of determinations carried out by the same person in as nearly as possible the same way shows slight discrepancies. The larger the number of determinations, the smaller will be the deviation of their mean from the true value. (2) Those which are avoidable, arising from want of care in carrying out the work, including the use of unsuitable or faulty apparatus, or from the lack of manipulative skill on the part of the worker, or from errors associated with the method of the analysis employed. These last can often be partially eliminated or allowed for. For instance (*a*) error due to the solubility of a precipitate may be calculated or reduced by the common ion effect ; (*b*) error due to adsorption of some soluble substance on the precipitate may be prevented by previous removal of such substance ; (*c*) error due to the formation of a colloidal solution during the washing of a precipitate can usually be prevented by washing with a solution of a suitable electrolyte ; (*d*) error due to the variation in the composition of a precipitate under slightly different conditions of formation can be reduced by controlling such conditions as carefully as possible. Errors can often be allowed for by carrying out a determination under the same conditions using a known amount of the substance being determined, which is as nearly as possible equal to that in the sample being analysed. This is known as a check or control analysis. In certain cases where impurities in the reagents used might give rise to error, a blank determination is made under similar conditions, but the substance which is to be determined in the unknown sample is omitted in this blank test.

Amount of Substance required for Analysis, and Limits of Allowable Error

After the experimental errors have been reduced to a minimum, the percentage error in the final result depends on the amount of substance taken for the analysis. In volumetric

analysis the error in the measurement of the volume of the liquid delivered by the burette varies from 0·01 to 0·05 ml. Taking the higher limit and assuming that only 5 ml. of the solution in the burette is required, the error is equivalent to 1 per cent.; but if 25 ml. is required, the same error in the measurement represents a percentage error of only 0·2. As a general rule, then, the amounts taken should be such that from 20 to 30 ml. of the solution in the burette is required for each measurement. The total error in volumetric analysis by an accurate method should not exceed 0·3 per cent.

In simple gravimetric analysis, the amount of substance taken should be sufficient to give from 0·2 to 0·5 gram of precipitate in the final weighing. The unavoidable error arising in the course of the work should not, in general, exceed 1 milligram. One milligram represents an error of 1 per cent. if the weight of the whole precipitate is 100 milligrams, but only 0·2 per cent. if the precipitate weighs 500 milligrams. The amount of substance taken, therefore, should not be too small. With bulky, flocculent precipitates, like ferric hydroxide, which are difficult to filter and wash, an amount to give about 0·2 gram of precipitate is desirable; whereas with precipitates like silver chloride or barium sulphate, 0·5 gram, or even 1 gram if need be, is easily dealt with.

In the complete analysis of a complex substance, such as a rock, in which many constituents are present in widely varying proportions, no general rules can be given here; an amount varying from 0·5 to 2 grams is usually suitable.

Expression of Results

Care should be taken in expressing the final result of an analysis to avoid giving more significant figures than are justified by the known accuracy of the data. The significant figures of a number are those which commence with a figure other than a nought. The accepted practice is to include in the final result no more significant figures than the first doubtful one. For example the quantity 3·148 grams means that the weight is nearer 3·148 than 3·147 or 3·149 grams. The expression 4·8600 has five significant figures, but a single nought before the decimal point followed by one or more noughts just after it do not count as significant figures as they

are only used to fix the decimal place, and would disappear if different units were used in expressing the quantity, *e.g.* 0·0079 grams could be written 7·9 milligrams. If the figure 6 is the first doubtful one in the expression 25,600 grams, this quantity should be written 25·6 kilograms.

No result should be expressed to a greater number of figures than the number of significant figures in any quantity entering into the calculation. For instance, in calculating the parts per hundred thousand of chlorine in a sample of water, if 5·3 ml. of N/10 silver nitrate were required in titrating 200 ml. of the sample, the calculation should be shown as $5{\cdot}3 \times 0{\cdot}00355 \times \frac{100{,}000}{200} = 0{\cdot}94$ parts of chlorine per 100,000. The result should not be expressed beyond two significant figures, since the volume of silver nitrate in this type of titration cannot be determined to more than two significant figures. There is no advantage in using the figure 0·0035457 for the weight of chlorine equivalent to 1 ml. of N/10 silver nitrate, and calculations may often be simplified by rounding off the figures in the more accurately known quantities.

SOLUTION OF THE SUBSTANCE

Provided the nature of the substance and solvent allows, the substance is brought into solution in the vessel in which the next operation is to take place. As a rule, either a beaker, a flask, or a porcelain basin is suitable.

With regard to the choice of vessels for quantitative analysis, it should be remarked that the solvent action on glass of water, acids, and more especially alkaline solutions, is considerable, and in precise work it cannot be neglected. The amount dissolved depends on the nature of the glass, and increases with the temperature and with the length of time the glass and liquid are in contact. It is considerably less in the case of glass vessels that have been in use for some time. Porcelain and borosilicate glass resist the action of solvents much better than ordinary glass, and should be used as far as possible in preference to the latter.

If precipitation is to follow solution, the weighed substance is brought into solution in a beaker. Solution may be promoted, if necessary, by heating the beaker (supported on wire gauze)

with a Bunsen flame, or by warming on a steam-bath. If actual boiling is required, or if gases are evolved, loss of substance by spirting or spray is prevented by covering the beaker with a clock-glass (Fig. 8). The clock-glass should be, at most, half an inch larger than the mouth of the beaker, and, in order to provide an outlet for steam or escaping gas, the beaker should have a spout. If evaporation is to follow solution, a porcelain basin is used, also covered with a clock-glass of suitable size. In the case of a flask, loss of substance is prevented by placing a small funnel in the mouth of the flask (Fig. 9), or by clamping

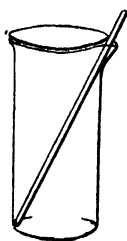



FIG. 8.

FIG. 9.

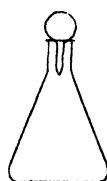



FIG. 10.

the flask in a sloping position. A flask should be used, as a rule, if prolonged heating with volatile acids is necessary, and in this case a glass bulb may be placed in the mouth of the flask (Fig. 10).

After solution is complete, or decomposition ended, the cover of the vessel must always be rinsed with a jet of water from the wash-bottle, and the washings added to the solution.

EVAPORATION

In this operation three points demand special attention, viz.:—

(1) No loss of substance must occur in the process.
(2) It should take place as rapidly as possible—with due regard to point 1.
(3) Contamination from without must be guarded against.

Loss of substance is prevented by evaporating on the steam-bath, thus avoiding actual ebullition of the liquid. As a rule, the process should be conducted in a porcelain basin, not more than two-thirds filled; in a beaker evaporation is

slow. Dust, etc., is excluded by placing over the basin a clock-glass, of larger diameter than the basin, supported, *convex side upwards*. This may be held in a clamp, or rest upon a glass tripod made for the purpose. A better device which conveys vapour away more rapidly, and prevents any condensed liquid dropping on to the water-bath, is shown in Fig. 11.

The rate at which evaporation proceeds depends on the continuous removal of the vapour over the surface of the liquid by means of a current of air, and the operation should therefore be conducted in a good draught. A large excess of steam must be carefully avoided.

It is sometimes necessary to conduct evaporation on a steam-bath in such a manner as to protect the contents of the basin

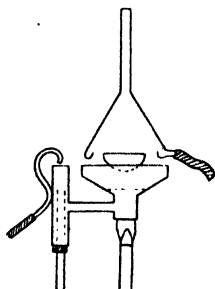
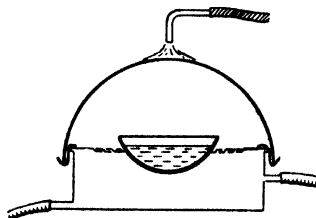



FIG. 11. FIG. 12.

from contamination with impurities, such as sulphur dioxide (from coal-gas flames), ammonia, etc., in the laboratory atmosphere. For this purpose, the arrangement shown in Fig. 12 is both simple and efficient. The hemispherical condensing cover may be of glass (an inverted glass basin), or, better, of thin copper. One half of a cistern " ball-cock " float, 15 to 20 cm. in diameter, makes a satisfactory cover and is easily obtainable. The glass or copper cover is cooled by a stream of tap water, and an external source of steam is used. Evaporation by this method is rapid and, on this account, the arrangement may be used in place of the ordinary plan if a good draught is not available.

Evaporation at the boiling-point may be conducted in a flask, supported obliquely and only half filled. This method is also useful if effervescence due to the escape of gas occurs on heating.

A modern method of evaporating liquids is to suspend an electrically heated unit *above* the surface of the liquid. The radiated heat produces evaporation without the accompaniment of bumping or creeping of separated solids.

Electrically heated baths are also used for the evaporation and distillation of inflammable liquids. Gas or electrically heated thick metal plates are useful for evaporation purposes, the temperature gradient being made use of for varying the speed of evaporation.

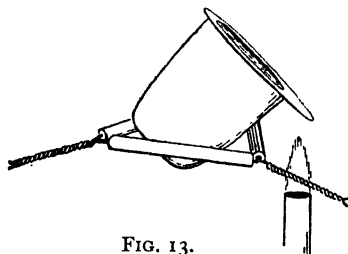



FIG. 13.

Evaporation of Sulphuric Acid.—The evaporation in a platinum crucible of a liquid of high boiling-point, such as concentrated sulphuric acid, is conducted with a free flame. In order to avoid loss by spirting and to prevent the liquid from creeping up the side and over the rim, the covered crucible is supported obliquely on a pipe-clay triangle, and the tip of the lid is heated with a small flame (Fig. 13). As the evaporation proceeds the flame may be brought under the rim of the crucible, but care must be taken that the heating is not too rapid.

Another arrangement is to place the crucible within a capacious iron, nickel, or porcelain crucible fitted with an asbestos ring or an appropriate triangle of iron wire wrapped with platinum foil (Fig. 42, p. 213). The outer crucible, without a cover, is heated over a moderately low flame and forms a hot air-bath which ensures uniform heating of the platinum crucible within.

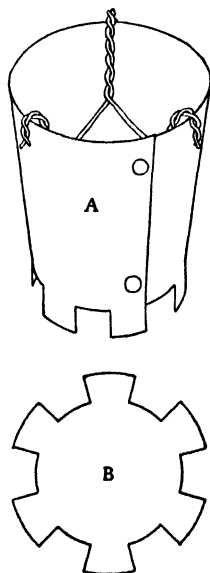



FIG. 14.

A useful form of air-bath is shown in Fig. 14. It can

easily be made in the laboratory workshop from sheet iron or nickel. The joint is riveted and the base B is secured to A by *bending the notched edges over one another.* A *convenient size is 7 cm. high, 7 cm. wide at the top, and 5 cm. at the bottom.*

PRECIPITATION

This is generally conducted in beakers. Conical flasks are sometimes preferable, but round flasks are unsuitable. Resistance-glass or porcelain vessels should be used in preference to ordinary glass vessels for precipitations with alkali hydroxides and carbonates and with ammonia. The following general considerations regarding precipitation in quantitative analysis may be noted :—

(1) The precipitate must be of known composition, or must be capable of conversion into a substance of known composition.

(2) The precipitation must, of course, be as complete as possible, and the precipitate must be in such a condition that it can be filtered and washed in reasonable time.

By choosing suitable conditions under which the precipitation takes place, the character of the precipitate can be controlled to a considerable extent. By avoiding a high degree of supersaturation, the number of primary particles can be kept relatively small ; and this enables them to grow to dimensions which ensure easy filtration. If concentrated solutions of the precipitants are rapidly mixed, a very large number of minute particles separate at once, with the result that a colloidal solution may be produced.

The aim should be to commence the precipitation under conditions of maximum solubility, and gradually to change the conditions so as to decrease the solubility. These conditions can often be attained by suitably adjusting the hydrogen ion concentration, by selecting a suitable temperature for precipitation (most precipitates being more soluble at higher temperatures), and by the gradual addition of one precipitant to a much diluted solution of the other.

A low degree of supersaturation can also be attained by

FIG. 15. Filtration and Washing by Decantation.

FIG. 16.—Transferring the Precipitate to the Filter.

[Face page 31

slowly running solutions of both precipitants into water with continuous stirring.

The conditions are finally altered to bring about as complete precipitation as possible, and in such a manner that the particles are allowed to grow in size. For example, in the case of calcium oxalate, if the precipitation is brought about in an ammoniacal solution, a fine precipitate, difficult to filter, is obtained. If ammonium oxalate, however, is added to a solution slightly acidified with hydrochloric acid, gradual addition of ammonium hydroxide to the boiling solution then produces a precipitate in granular form.

In most cases it is advisable to allow the precipitate to stand some hours before filtering. This not only causes more complete precipitation, but enables the large crystals to grow at the expense of the smaller ones. Moreover, it has been established that aged precipitates are less contaminated by adsorbed ions than those which have just been precipitated.

(3) The precipitate must be free from contamination with other substances.

In spite of all precautions to prevent it, partial precipitation of small amounts of one or more other substances in addition sometimes occurs. In such cases it is often possible to effect a more or less complete separation by redissolving the precipitate after filtration, and precipitating a second time. As a rule, a slight excess of the reagent must be added ; a large excess is, however, generally prejudicial, and is a common source of error. The reagent should be added carefully, a little at a time, until, after allowing the precipitate to settle, it is seen that another drop causes no further precipitation.

FILTRATION

In quantitative analysis, filtration must be conducted with much greater care than is sometimes given to the operation in qualitative analysis. The more important rules to be observed are the following :—

(1) The *size* of the filter depends, not on the volume of the liquid, but on the bulk of the precipitate to be separated. The precipitate must not more than half-

fill the filter. As a rule, a filter paper 9 cm. in diameter is large enough, but for bulky precipitates an 11-cm. paper is required.[1]

(2) The filter paper when folded must be somewhat smaller than the funnel, *e.g.* a 9-cm. paper requires a funnel 5·5 cm. in diameter.

(3) It is most important that the folded paper should fit the funnel properly. If the funnel angle is not exactly 60°, the paper must be folded with a certain amount of overlap at the second fold so that one cone is larger than the other. In this way a cone of the appropriate size can be obtained. The paper is then held in place in the dry funnel, and, after wetting with water, is well pressed into contact with the funnel wall, especially round the top. This will prevent the entrance of air, and if the stem of the funnel once fills with liquid it will remain full, and the slight suction will effect more rapid filtration.

(4) If possible, liquids should be filtered hot.

(5) The underside of the rim of the beaker containing the precipitate should be rubbed at one place with an almost invisible trace of melted rubber[2] or vaseline and at this place the liquid should be poured down the stirring-rod into the filter, directing the liquid against the side of the filter and not into the apex (Fig. 15). The level of the liquid must not approach nearer than 0·5 cm. to the edge of the paper.

(6) In order to prevent loss by splashing, the stem of the funnel must rest against the side of the receiving vessel.

[1] A special quality of filter paper which has been extracted with hydrochloric and hydrofluoric acids—so-called "ashless" paper—must be used in quantitative analysis. The ash of a single small filter weighs about 0·1 mgrm., and is negligible. Several varieties of "ashless" filter papers are made; for flocculent precipitates, like ferric hydroxide, an open texture paper which filters very quickly is desirable, whereas a paper of closer texture is usually required for fine precipitates like barium sulphate or calcium oxalate.

[2] Obtained by heating the end of a scrap of rubber tubing in a flame.

Washing of Precipitates.—In washing precipitates the aim should be to free the precipitate from dissolved substances with the minimum amount of the washing liquid, in order to reduce loss of the precipitate by solution, and to avoid obtaining too large a volume of filtrate if this should be required later. The washing liquid should be chosen so that it has a minimum solvent effect on the precipitate, and does not peptise it even after electrolytes have been washed out. If the precipitate is to be weighed either after drying at a suitable temperature or after ignition the final washing liquid must not leave a weighable residue, nor must it cause any volatilisation of the precipitate if this is to be ignited, *e.g.* it is better to use a solution of ammonium nitrate than ammonium chloride in washing ferric hydroxide, since some ferric chloride might be formed and volatilised in the latter case.

To fulfil these requirements the washing liquid must be chosen in accordance with the properties of the particular precipitate being treated. Water alone may be satisfactory in many cases, but when electrolytes have been almost washed out of the precipitate there is often a tendency for the formation of a colloidal solution which passes through the filter. This effect is prevented by the use of a solution of an electrolyte such as ammonium chloride or nitrate, which leaves no residue on ignition, but neither could be used as the final washing liquid when the precipitate was to be weighed after drying only. In the latter case an organic solvent is usually employed as the final washing liquid, *e.g.* acetone or alcohol followed by ether. To reduce the solubility of the precipitate in the washing liquid, a solution having an ion in common with one in the precipitate is often employed. For instance, in determining lead as sulphate, the precipitate is washed at first with normal sulphuric acid, in which it is almost insoluble. The solution having the common ion must, however, not be too concentrated in case there is a tendency to form a complex ion which would have the effect of greatly increasing the solubility of the precipitate. A washing liquid which at first sight would appear to be ideal is a saturated solution of the precipitate itself. Theoretically, however, this might lead to obtaining high results, because if the saturated solution is used before first washing out excess of the precipitant the latter would tend to precipitate some solid from the saturated solution used for

washing. Actually in the case of very sparingly soluble precipitates this would not introduce any serious error. For instance in the case of calcium oxalate, the solubility is approximately 6 mgrms. per litre of water at 18°. If 25 ml. of the saturated solution was used in washing the first time by decantation, and if the excess of ammonium oxalate present in the precipitate caused complete precipitation of the calcium oxalate in the 25 ml. of solution (which would certainly not be the case even on long standing) this would only amount to $\frac{6}{40} = 0{\cdot}15$ mgrms. During the subsequent washings still less would separate since the concentration of the ammonium oxalate would be much reduced.

If there is no marked increase in solubility, considerable time may be saved by washing with a hot liquid, since hot liquids filter much more rapidly than cold ones.

Completion of the washing process should always be ascertained by collecting a few drops of the filtrate in a test tube, and testing for an ion such as chloride, if this was present during precipitation, but not contained in the washing liquid. Excessive washing must be avoided, as this would increase losses due to solubility.

Before commencing to filter allow the precipitate to settle; then, without disturbing the precipitate, pour as much as possible of the clear liquid into the filter.

If the precipitate settles without long standing, it is much more satisfactory to wash it several times by "decantation" than to transfer it at once to the filter. This is carried out as follows:—After the supernatant liquid has been poured through the filter, add 25 to 60 ml. of the washing liquid and stir thoroughly (the former volume being sufficient for a precipitate which settles to a compact mass). Allow the precipitate to settle again, and once more decant the clear liquid into the filter; repeat the process two or three times. Washing by decantation ensures that all portions of the precipitate come into intimate contact with the washing liquid, which is not the case if washing is carried out on the filter. This applies particularly to gelatinous precipitates, in which crevices and channels are formed, and the washing liquid does not reach portions of the precipitate between these channels. Washing by decantation tends to give bulky filtrates if the

precipitate does not settle well, but in most cases it results in more satisfactory washing than can be attained on the filter alone. It may usually be omitted if the precipitate is very small.

In order to reduce the total volume of washing liquid as far as possible, the following considerations should be borne in mind. Repeated washing with small volumes of liquid is much more effective than the use of the same total volume applied in one or two stages. Another important factor is that the liquid added each time to the filter should be allowed to drain through as completely as possible before adding the next lot. These points may be made clearer by a particular case. Suppose that at each washing the precipitate retains 3 ml. of liquid, and that 27 ml. of washing liquid are added each time, the concentration of the dissolved impurities will be reduced at each stage by 1/10 of their previous value, provided that the precipitate is merely mechanically contaminated and has not adsorbed dissolved substances. Therefore, after four such stages of washing the concentration of the dissolved substances will have been reduced to 1/10,000 of their original value. If the total 108 ml. of washing liquid had been used in one operation, the concentration of the dissolved substances left in the precipitate would only have been reduced to 3/111 or 1/37 of the original. If, on the other hand, four stages of washing were carried out, but in this case leaving 6 ml. with the precipitate each time, this would leave the precipitate with a concentration of dissolved substances of $\left(\frac{6}{33}\right)^4 = \frac{1}{915}$ of their original value, showing that the washing is much less complete than in the previous case of four stages of washing when the precipitate was more effectively drained.

After washing by decantation, transfer the precipitate to the filter by means of a jet of water from the wash-bottle in the manner shown in Fig. 16. Remove any precipitate adhering to the side of the beaker by means of a stirring-rod tipped with a piece of *black* rubber tubing, 2 cm. long.[1]

Wash the precipitate on the filter, bearing in mind the above instructions, and taking care to wash the margin of the

[1] Short rubber tubes, closed at one end, are obtainable for this purpose. Rubber-tipped rods should not be used as stirring-rods and should not be allowed to remain in solutions.

filter paper each time. Be careful not to use so strong a jet of water, or to direct it in such a way, that portions of the precipitate are projected out of the filter. Towards the end of the process endeavour to collect the precipitate as far as possible in the apex of the filter.

Never put anything but distilled water in the wash-bottle. Separate small wash-bottles (300 ml.) should be used for ammonia, hydrogen sulphide, alcohol, etc. In order to prevent the backflow of ammonia, etc., to the mouth, a valve may be used. To make the valve, a slit (1 cm.) is cleanly cut in a piece of narrow rubber tubing (3 cm.). One end of the rubber tube is closed with a plug of glass rod, and the valve is then attached to the blow-tube inside the wash-bottle (Fig. 17).

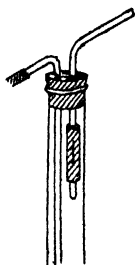



FIG. 17.

Use of the Filter-Pump.—Accelerated filtration, by means of the filter-pump, is frequently advantageous, especially in the case of bulky, gelatinous, or slimy precipitates like aluminium or chromic hydroxides, or zinc sulphide. The platinum cone which is used to support the filter paper must be well made and in good condition ; a bad cone with rough edges is often itself the cause of rupture of the filter paper. In place of a platinum cone, one of toughened paper may be used. Gentle suction only should be used,[1] and the suction should be interrupted as soon as all the liquid has passed through. To effect this most simply without stopping the pump, the latter is connected to the filter-flask through a T-piece, one limb of which is closed by a piece of rubber tubing and clip (Fig. 18). When necessary, the clip is opened to admit air. If any cracks or channels form in a bulky precipitate (the result of continuing suction after all the liquid has passed through), close them carefully with a jet of water or with a glass rod.

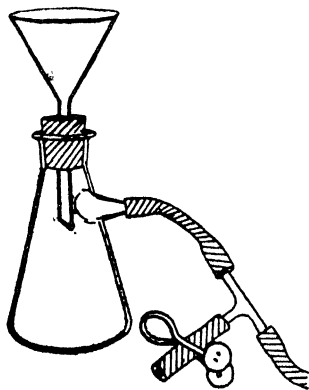



FIG. 18.

Instead of the filter-pump, it is often more convenient to

[1] A pressure regulator for use with the filter-pump is described on p. 213.

use a funnel provided with a looped suction-tube about 20 cm. long and 4 to 5 mm. internal diameter. The funnel stem is cut short, and the suction-tube fused on, as shown in Fig. 19.

In using either the filter-pump or a suction-tube it is most important that the filter paper should fit the funnel properly, and that no air can leak along the folds of the paper at either side. If air-leakage sets in, the edge of the paper should be firmly pressed into contact with the funnel by means of the stirring-rod. Once suction has been established with a suction-tube, the filter should not be allowed to empty until all the liquid has been filtered.

Paper-pulp Filter.—It is sometimes convenient to filter through paper-pulp, instead of using an ordinary filter paper. A paper-pulp filter is prepared as follows :—Tear a 9-cm. filter paper into small pieces and shake the paper with dilute nitric acid in a small flask until it is completely disintegrated. Place a perforated porcelain disc about 2 cm. in diameter in a 7-cm. funnel, cover the disc with a circle of filter paper, and pour the pulp on the disc, using gentle suction (Fig. 18). Press the pulp down gently with a flat ended glass rod or with the finger, and wash it with warm water until free from acid. A small Büchner funnel (Fig. 4, p. 19) may be used instead of an ordinary funnel and perforated disc.

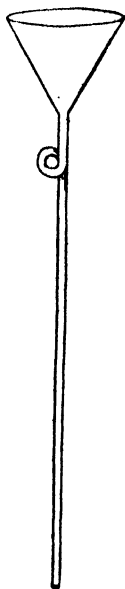



FIG. 19.

PART II

VOLUMETRIC ANALYSIS

VOLUMETRIC methods of analysis, although based on a great variety of chemical reactions, present certain common features, and a quantitative determination by volumetric methods usually involves :—

(1) The preparation of one or more solutions of accurately known concentration ;
(2) The use of instruments by means of which the volumes of the solutions employed can be quickly and accurately measured ;
(3) Some means of recognising the completion of the chemical change involved.

Many volumetric methods are of great practical value on account of their simplicity, rapidity, accuracy, and wide applicability. The following example, omitting certain experimental details, illustrates the general features of a simple determination.

Suppose it is required to determine the amount of sodium chloride in a given solution. A solution of silver nitrate of known concentration is prepared by dissolving an accurately weighed amount of pure silver nitrate in water and making up the solution to a definite volume. A suitable quantity of the sodium chloride solution is accurately measured into a stoppered bottle, a little nitric acid is added, and the silver nitrate solution is run in, in small portions at a time. After each addition of the silver nitrate solution, the mixture is vigorously shaken in order to coagulate the silver chloride and leave the supernatant liquid clear. It is then easy to observe that, when all the chloride has been converted into silver chloride, the addition of another drop of silver nitrate solution produces no further precipitate. This point is called the " end-point " of the reaction. The process involved in the

comparison of one solution with another by a volumetric method such as this is called " titration."

In this way it is possible to determine accurately the *volume* of silver nitrate solution necessary to precipitate all the chloride. Now this volume of silver nitrate solution contains a definite *weight* of silver nitrate which can readily be calculated since the concentration of the silver nitrate solution is known ; and since 169·9 grams of silver nitrate interact with 58·46 grams of sodium chloride, it is easy to calculate the amount of sodium chloride in the solution once the weight of silver nitrate equivalent to it is known.

Standard Solutions.—Any solution of accurately known concentration is called a *standard* solution. Standard solutions may sometimes be prepared by dissolving an accurately weighed quantity of the substance in water and making the solution up to a definite volume ; *e.g.* standard solutions of silver nitrate and sodium carbonate may be prepared in this way. Often, however, the material to be used contains an unknown amount of impurity, or may be found unsuitable for weighing because it is deliquescent or efflorescent. In such cases, a solution of approximately the required concentration is prepared, and the exact concentration is then found by titration against some suitable substance. For example, a standard solution of sulphuric acid may be prepared by making a solution of approximately the desired concentration on the assumption that the concentrated acid contains 96 per cent. by weight of H_2SO_4, and then finding the exact concentration by titration against accurately weighed quantities of pure sodium carbonate.

Normal Solutions. — For the sake of uniformity and especially for convenience in calculations, it is desirable to prepare standard solutions that contain one gram-equivalent (or a simple fraction of the gram-equivalent) of the reacting substance per litre. A solution that contains one gram-equivalent of the reacting substance per litre of solution is called a *normal* solution.

The gram-equivalent of a substance is the weight of the substance, in grams, that is chemically equivalent to 8 grams of oxygen, or to 1·008 grams of hydrogen.

A normal solution of hydrochloric acid (which is monobasic) therefore contains 36·47 grams (the gram-molecular weight, or molar weight) of HCl per litre ; a normal solution

of sulphuric acid (which is dibasic) contains 49·04 grams (half the molar weight) of H_2SO_4 per litre; and normal solutions of sodium hydroxide and sodium carbonate contain, respectively, 40·00 grams of NaOH and 53·00 grams of Na_2CO_3 per litre.

Many important volumetric methods are based on oxidation and reduction processes, and a normal solution of an oxidising agent is one that is capable of yielding one gram-equivalent, or 8 grams, of "available" oxygen per litre. Potassium permanganate is an example of an oxidising agent which is used in volumetric analysis for the determination of various oxidisable substances. Titrations with potassium permanganate are carried out in presence of an excess of dilute sulphuric acid, and, as the following equation shows, only part of the oxygen of the permanganate is "available" oxygen:

$$2KMnO_4+4H_2SO_4 = 2KHSO_4+2MnSO_4+3H_2O+5[O].$$

Of the 8 oxygen atoms in $2KMnO_4$, only 5 are "available" for the oxidation of the reducing substance present. Since $2KMnO_4$ (316·1 grams) yields 5[O], or 80 grams of available oxygen, a normal solution of potassium permanganate, used as an oxidising agent in the manner indicated, will contain 316·1/10 = 31·61 grams of the salt per litre.

It is important to realise that, as in the case of potassium permanganate, the chemical equivalence of one and the same substance sometimes varies with the type of interaction in which it plays a part. Potassium tetroxalate, for example, may be used for standardising sodium hydroxide solution (see p. 80), and the gram-equivalent is *one-third of the molar weight*, or 84·7, because the molecule, $KHC_2O_4, H_2C_2O_4, 2H_2O$, contains three replaceable hydrogen atoms; but if the salt is to be used as a reducing agent for standardising potassium permanganate solution (see p. 105), *one-fourth of the molar weight*, or 63·55 grams, is equivalent to 8 grams of oxygen (or 1 litre of normal permanganate solution) because the oxidation of the molar weight requires 32 grams of oxygen.[1]

Normal solutions are found to be too concentrated for many

[1] In the case of a substance which has a different equivalent weight in different reactions, it is advisable, in addition to the normality for the usual reaction, to label its solution also in terms of *molarity*, *i.e.* the number of gram-molecules of the substance per litre of its solution.

purposes, and more dilute standard solutions, which may be *seminormal*, *decinormal*, etc., are then used instead. When a standard solution is not exactly normal, the concentration is always expressed in terms of a normal solution. Thus, a solution of hydrochloric acid containing 36·76 grams of HCl per litre is $\frac{36\cdot76}{36\cdot47} = 1\cdot008N$; and a solution of potassium permanganate containing 3·145 grams of $KMnO_4$ per litre is $\frac{3\cdot145}{31\cdot61} = 0\cdot0995N$, the symbol "N" being used as a contraction for normal.

Determination of the End-Point in a Titration

Various means are available for determining the end-point in a titration. These may be classified as follows :—

(1) A permanent precipitate is formed, *e.g.* as in the titration of potassium cyanide with silver nitrate.

(2) A precipitate just ceases to be formed, *e.g.* as in the titration of silver nitrate with sodium chloride (without potassium chromate).

(3) A faint tint is obtained throughout the titrated solution, owing to the addition of a slight excess of a solution which possesses a strong colour ; *e.g.* as in titrations with potassium permanganate.

(4) A colour change is produced by the addition of a slight excess of the added solution in a substance called an "indicator," which may be mixed with the titrated solution, or used externally. Such indicators include those used in acidimetry and alkalimetry, and substances such as starch, potassium ferricyanide, potassium chromate, uranium acetate, etc.

(5) A sudden change is produced in the electrical conductivity of the titrated solution, as in acidimetry and alkalimetry, and in certain precipitation analyses.

(6) A rapid alteration is produced, by a series of small additions of a reagent, in the potential difference between a suitable electrode immersed in the titrated solution and a standard electrode. This method is

used in acidimetry and alkalimetry, and in oxidation and reduction reactions.

(7) The appearance or disappearance of fluorescence in a solution, to which a suitable organic substance has been added, this being occasioned by a very small change in the hydrogen ion concentration of the solution. Using ultra-violet light acid-alkali titrations can be carried out in highly coloured or turbid solutions.

The method selected will depend on the type of reaction involved, and on any interfering substances present. For instance, in the case of a solution of acid or alkali which contains coloured impurities, an electrometric method may give a much more satisfactory result than one involving the use of indicators.

It will be noticed that in several of the above methods a slight excess of the added reagent is necessary. In these cases, the end-point of the titration will not correspond exactly with the stoichiometrical or equivalent point as required by the equation for the reaction. The excess can be determined approximately by ascertaining the volume of the titrating liquid required to produce the necessary changed colour in the indicator, when this alone is present in a volume of liquid equal to that of the final volume of the titrated solution.

As the matching of the final tint may be uncertain, a more accurate result may be obtained by making a series of titrations using different volumes of the titrated liquid, say in the ratio 1 : 2·5 : 5 (10 ml., 25 ml., and 50 ml.), working to the same final tint in each case. Then if x is the excess required, and V_1, V_2, and V_3 are the observed volumes run in from the burette, V_0 being the correct volume required for 10 ml., $5V_0+x = V_3$; $2{\cdot}5\,V_0+x = V_2$; $V_0+x = V_1$. From these equations a mean value for V_0 can be calculated.

THE MEASUREMENT OF VOLUMES OF LIQUIDS

For the measurement of the volume of a liquid, various graduated glass instruments are used, the most important being *pipettes*, *burettes*, and *graduated flasks*. *Measuring cylinders* are used for rough measurements only.

Flasks.—Flasks are used in volumetric analysis mainly for the measurement of comparatively large volumes, *i.e.* for volumes of 100 ml. and upwards. A flask is usually graduated to *contain* a definite volume of liquid.

Pipettes.—A pipette is used to *deliver* one specified volume of liquid. Pipettes are made in various sizes, from 1 ml. up to 100 ml. or more. The 10 ml. and 25 ml. are the most generally useful sizes.

Burettes.—A burette is used to deliver, not a fixed volume of a liquid, but any specified volume up to its total capacity. For ordinary work a 50 ml. burette is commonly used.

The Unit of Volume

The fundamental unit used in measuring the volume of a liquid is the **litre.** The litre is defined, not as a cubic decimetre (the original definition) but as the volume occupied by one kilogram [1] of water at its temperature of maximum density, and subjected to the normal atmospheric pressure. The apparent weight in air of water which occupies one litre at the temperature of maximum density will be less than one kilogram, because of the effect of the buoyancy of air. The apparent weight will be still less when the determination is made at ordinary room temperature, because of the then lower density of water. These factors must be allowed for in determining the volume of a piece of apparatus by weighing the water it contains or delivers. The thousandth part of a litre, *i.e.* a **millilitre,** is not exactly equal to a thousandth part of a cubic decimetre, *i.e.* a **cubic centimetre,** but for all practical purposes the difference is entirely negligible.[2]

An effort is being made in all countries to replace the cubic centimetre by the millilitre, not because of the minute error involved, but to avoid the haphazard use of the term cubic centimetre for three different meanings, (1) the true cubic centimetre, (2) the true millilitre, (3) the unit of volume as

[1] The standard kilogram (originally defined as the mass of a cubic decimetre of water at 4° C.) is now, for all purposes, identified with the platinum "Kilogramme des Archives" (kept in Paris) in its actual state.

[2] The litre, as defined by reference to the standard kilogram, has been found by direct experimental determination to be equal to 1000·027 c.c., *i.e.* 1 ml. is equal to 1·000027 c.c.

defined by Mohr, which is the volume at 60° F. of that quantity of water which, when weighed in air with brass weights, has an apparent weight of one gram. This unit, denoted "G.W.A." (grams of water in air), is as much as 0·2 per cent. larger than the millilitre, *i.e.* 1000 G.W.A. equals 1002 ml. It is rarely used now. The British Standards Institution now uses the millilitre in all British Standard Specifications. As it is obviously desirable to use a fraction of the universally accepted larger unit, rather than one derived from an entirely different system, the millilitre is used instead of the cubic centimetre throughout the present edition of this book.

Measuring instruments as bought may be inaccurate. The experimental determination of the errors in the graduation of the instrument is called *calibration*. If the graduations are altered or adjusted so as to make the instrument accurate, it is said to be *standardised*. Graduated instruments, the accuracy of which has been determined at the National Physical Laboratory,[1] Teddington, may now be obtained. Two classes of tests are made at the Laboratory, Class A tests for apparatus to be used for work requiring great accuracy, and Class B tests for apparatus intended for ordinary use. The limits and tolerances allowed for these two grades are given under the descriptions of the various instruments. For a capacity not given in any table, the data corresponding to the next larger capacity must be taken. The instruments are marked with the Laboratory monogram, NPL, the class to which they belong, and the year of testing. Measuring instruments of ordinary commercial quality should be standardised or calibrated by the user.

Since the volume of a glass vessel varies with the temperature, it is necessary to select some definite temperature at which the vessel will hold the volume marked upon it. In this country 20° C. has been chosen as the standard temperature, and is marked on the apparatus by the makers.

In order to determine the volume delivered by or contained in a piece of apparatus, it is necessary to weigh the water delivered by or contained in it at some particular

[1] The Laboratory regulations are given in detail in the pamphlet *Tests on Volumetric Glassware*, which may be obtained, free of charge, on application to the Director, The National Physical Laboratory, Teddington, Middlesex. By courtesy of the Laboratory this pamphlet has been largely drawn upon for the information in the following pages.

temperature, preferably near to the standard temperature. It is then necessary to calculate what the volume of the water so weighed would be at the standard temperature, making use of the known values of the density of water at different temperatures, and applying corrections for the effects of the buoyancy of air and the expansion or contraction of the glass, if this is at a temperature other than 20° C.

By using the table below these calculations may be avoided. The figures corresponding to the particular temperature and volume concerned indicate the number of grams to be added to the weight in grams of water contained in or delivered

t° C.	Nominal capacity of vessel in millilitres.								
	5.	10.	20.	25.	50.	100.	250.	500.	1000.
10	0·008	0·016	0·031	0·039	0·079	0·157	0·390	0·79	1·57
11	0·008	0·016	0·033	0·041	0·083	0·165	0·410	0·83	1·65
12	0·009	0·017	0·035	0·044	0·087	0·174	0·435	0·87	1·74
13	0·009	0·018	0·037	0·046	0·092	0·184	0·460	0·92	1·84
14	0·010	0·020	0·039	0·049	0·098	0·195	0·490	0·98	1·95
15	0·010	0·021	0·041	0·052	0·104	0·207	0·520	1·04	2·07
16	0·011	0·022	0·044	0·055	0·110	0·220	0·550	1·10	2·20
17	0·012	0·023	0·047	0·059	0·117	0·234	0·585	1·17	2·34
18	0·012	0·025	0·050	0·062	0·125	0·249	0·620	1·25	2·49
19	0·013	0·026	0·053	0·066	0·133	0·265	0·660	1·33	2·65
20	0·014	0·028	0·056	0·071	0·141	0·282	0·705	1·41	2·82
21	0·015	0·030	0·060	0·075	0·150	0·300	0·750	1·50	3·00
22	0·016	0·032	0·064	0·080	0·160	0·319	0·800	1·60	3·19
23	0·017	0·034	0·068	0·085	0·170	0·339	0·850	1·70	3·39
24	0·018	0·036	0·072	0·091	0·181	0·361	0·905	1·81	3·61
25	0·019	0·038	0·077	0·096	0·192	0·384	0·960	1·92	3·84

by a graduated vessel in order to obtain the numerical value of the volume in millilitres at 20° C.[1]

The corrections given in the table assume that the weighings are made in air at 760 mm. and 50 per cent. humidity. If the barometric height is not exactly 760 mm., an additional correction may be made for variation in air density. This correction is very small, however, and may be neglected in calibrating apparatus for work of ordinary accuracy. Thus for a litre flask at 20° C., the correction for a difference in barometric pressure of ± 30 mm. above or below 760 mm. is only ± 0·04 gram, which is only one-fifth of the N.P.L. Class A tolerance (± 0·2 ml.)

[1] A table corresponding to that given above, but at 15° C, the former standard temperature, is given on p. 485.

on a flask of this capacity. The correction for an extreme variation in humidity is even less.

The use of the table is illustrated by the following examples :—

(1) 34·91 grams of water at 18° C. were delivered by a burette between the 0 and the 35 ml. mark. From the table the total amount to be added in this case to the apparent weight is 0·025+0·062, *i.e.* 0·087. The required volume in mls. is therefore 34·91+0·087, *i.e.* 34·997 at 20° C.

(2) The table may also be used to find the amount of water at t° C. that must be weighed out to occupy a specified volume at 20° C. *E.g.* the water to be weighed out at 13° C. in the case of a 250 ml. flask is 250—0·460, *i.e.* 249·54 grams.

(3) When a solid is weighed, dissolved, and titrated with a solution the temperature of which is appreciably different from the standard temperature, a slight error will occur. This is due to the fact that the normality of the solution will change slightly on expansion or contraction. This small error may be calculated approximately by means of the table on p. 45. The difference between the correction for 20° and that for the temperature of the solution must be added to the observed volume used.

Thus in the case of a titration requiring 50 ml. at 11°, the true volume at the standard temperature would be approximately 50+(0·141—0·083), *i.e.* 50·06 ml.

This error will not arise when two dilute solutions at the same temperature are being titrated, since each will expand or contract almost exactly to the same extent.

STANDARDISATION OF A FLASK

The flask should be provided with a well-fitting ground-in glass stopper, and should have a long narrow neck (Fig. 20). The N.P.L. regulations [1] require that the graduation mark must be at least 3 cm. from the top of the neck of flasks of

[1] See N.P.L. pamphlet, *Tests on Volumetric Glassware.*

capacity 100 ml. or less, and at least 6 cm. from the top of the neck of flasks of capacity greater than 100 ml. The graduation mark must be at least 1 cm. above the point at which the neck begins to expand at the junction with the bulb on flasks of capacity 100 ml. or less, and at least 2 cm. above this point on flasks of capacity greater than 100 ml. There should be sufficient air space above the mark to allow of thorough mixing of liquids with a reasonable number of invertions and shaking of the flask.

The internal diameter of the neck at the graduation mark must not exceed the values given below for the two grades of flasks.

Capacity ml. . .	10	25	50	100	250	500	1000	2000
Diameter mm. .	6	8	10	12	14	16	20	25 for Class A.
Diameter mm. .	8	10	12	14	16	19	22	27 for Class B.

In addition to the graduation mark for "content," Class B flasks may also be so graduated that they will deliver a measured volume of liquid. Flasks intended for "delivery" are emptied by gradually inclining them, until, when the continuous stream of water has ceased, the neck is nearly vertical. In this position the flasks are allowed to drain for half a minute, during which time the edge of the neck is kept in contact with the inside of the receiving vessel, and at the end of the draining time any drop of water adhering to the edge of the neck is removed against the inside of the receiving vessel. Flasks graduated for "delivery" as well as "content" must bear the letter D above the upper mark and the letter C below the lower mark, and these marks must not be less than 1 mm. apart.

Clean the flask thoroughly,[1] and set it aside inverted until

[1] It is essential that volumetric apparatus be thoroughly clean before use. Deposits on the glass must be dissolved off by suitable reagents. The presence of grease will be shown by the formation of drops on the surface of the glass after liquid is run out. In this latter case, the vessel must be treated by one of the following methods until the surface remains uniformly wet after emptying.

(1) Grease may be removed by prolonged treatment with chromic acid solution, a mixture of roughly equal volumes of saturated potassium

it is dry, hastening the process by drawing through it a slow current of air by means of a water-pump. The process is much more rapid if the vessel is first rinsed with pure acetone. Weigh the flask on a suitable balance. (The weighing should be accurate to within 0·01 gram for a 100 ml. flask and to within 0·05 gram for a litre flask. A special balance, capable of supporting the heavy load, is required for flasks larger than 100 ml.) Fill the flask to the graduation mark with water preferably at a temperature of from 19° to 21°.

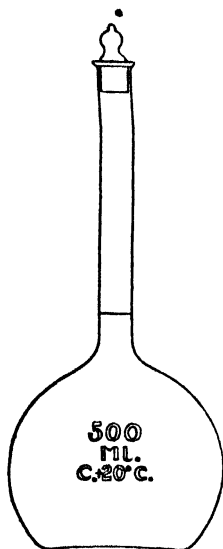



FIG. 20.

Examination of the surface of the water in the neck of the flask will show that it is not flat but curved, and the level of the water must be adjusted so that the *lowest* point of the curved surface (the meniscus) coincides exactly with the graduation mark. Error due to parallax is avoided when the front and back of the graduation mark are seen as a single line. The meniscus will be clearly visible if a white card is held behind it. The adjustment of the water level is made by first adding water to a few millimetres above the mark, but without wetting the sides of the neck above the water surface, and then removing water with a glass tube drawn out to a capillary.

Weigh the flask filled with water, and from the weight of the water, calculate the volume.

or sodium dichromate solution and concentrated sulphuric acid being used. This is slow but efficient. It is best to fill the vessel and set it aside overnight. A pipette may be kept full by filling almost to the top, inserting a length of rubber tubing fitted with a clip between the mouth and the pipette.

(2) A much quicker method consists in washing out the vessel with a few millilitres of benzene. After draining this off, a few millilitres of concentrated sulphuric acid are introduced, and this is similarly brought into contact with the whole surface, and then poured out. Subsequent washing with distilled water leaves a perfectly clean surface, unless the vessel has been exceptionally greasy, in which case the process must be repeated.

Example.—The following figures were obtained with a 500 ml. flask :—

Flask+water	=	565·85 grams
Tare of flask	=	65·20 ,,
Weight of water	=	500·65 ,,

The temperature of the water was found to be 14°. From the table on p. 45, it is seen that the weight to be added to the weight of water at 14° in the case of a 500 ml. vessel is 0·98 gram. The flask therefore contained 501·63 ml.

The flask may be used with application of the necessary correction, but it is more convenient to make a new graduation at the correct place. The position of this mark is found as follows :—Calculate the weight of water that will fill the flask to the correct graduation mark (in the above example, 500—0·98 = 499·02 grams). Place the calculated weight together with the tare of the flask on the balance-pan and adjust the amount of water in the flask until the total weight of the flask and water is found to be correct.

Etching a line on Glass.—A new line should then be etched on the glass at the correct position by means of hydrofluoric acid in the following manner :—Gum on two strips of paper completely round the tube, leaving only a narrow space between them where the line is to be etched (Fig. 21). Warm cautiously above a flame, and rub with a piece of paraffin wax until the paper is saturated with the melted wax. When it has solidified, remove the wax from the line between the two papers by means of a metal point. Fix a narrow strip of filter paper round this line, and wet the paper with hydrofluoric acid solution. (**Caution.**—Care must be taken that the hydrofluoric acid does not come into contact with the skin, since it causes later a particularly painful sore.)

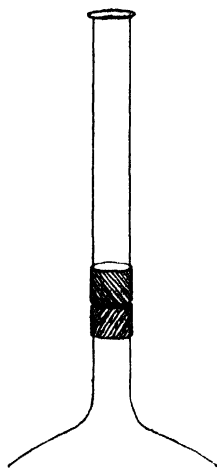



FIG. 21.

After about ten minutes, wash off the hydrofluoric acid and remove a small portion of the paper and wax to ascertain if the glass is sufficiently etched. If the etching is

insufficient, re-wax and repeat the process, but allow more time for the etching action.

The tolerances allowed on graduated flasks [1] are :—

Capacity ml.	10	25	50	100	250	500	1000	2000
Tolerance ± ml. for content								
Class A	0·015	0·03	0·04	0·06	0·1	0·15	0·2	0·4
Class B	0·02	0·04	0·06	0·1	0·2	0·3	0·4	0·6
Tolerance ± ml. for delivery								
Class B	...	...	...	0·2	0·4	0·6	0·8	1·0

USE AND STANDARDISATION OF A PIPETTE

The pipette should first be examined to make sure that it is capable of being used as an instrument of precision. The narrow tubes should not be above 4 mm. internal diameter for a 10 ml. pipette, 5 mm. for 25 ml. and 50 ml. pipettes, and 7 mm. for a 100 ml. pipette. The graduation mark [1] must be at least 6 cm. from the top of the suction tube of pipettes of capacity of 5 ml. or less, and at least 8 cm. from the top of the suction tube of pipettes of capacity greater than 5 ml. The suction tube of the pipette must be cylindrical for at least 1 cm. below the graduation mark on pipettes of capacity 5 ml. or less, and for at least 2 cm. below the graduation mark on pipettes of capacity greater than 5 ml.

A pipette will not deliver constant amounts if it discharges too quickly. The limits for the time of outflow for both Class A and Class B pipettes are shown in the following table [1] :—

Capacity ml.	1	2	5	10	30	50	100	150	250
Minimum delivery time in seconds									
Classes A and B	5	7	10	15	20	25	30	40	50
Maximum delivery time in seconds									
Class A	10	15	20	25	35	40	50	60	75
Class B	15	20	30	40	50	60	80	100	120

If the time of outflow is too short, the aperture may be reduced by heating the jet carefully in a flame until of the desired size. This method of adjustment, however, results in a sudden constriction at the jet, which is much less satisfactory than a gradual taper.

[1] N.P.L. pamphlet, *Tests on Volumetric Glassware.*

A pipette will not deliver a definite volume unless it is used in a specified manner, and the following instructions should be carefully followed.

See that the pipette is absolutely clean (see p. 47), and fill it by applying gentle suction with the mouth until the liquid is 3 to 4 cm. above the mark. Rapidly place the forefinger [1] over the top of the pipette and wipe the outside. Carefully allow a little air to enter past the finger until the bottom of the meniscus is in line with the mark on the pipette, which must be held vertically, and so that the mark is at the same level as the eye. The tip of the pipette should touch a clean glass surface during this process, so as to leave no adhering drop. Bring the receiving vessel under the tip of the pipette, remove the finger, and allow the contents to run out, while the tip is held in contact with the glass, which should be slightly inclined to the pipette.

10 ML. D·20°C 20+15 SEC

FIG. 22.—A Pipette.

After the continuous discharge has finished, the pipette must be allowed to drain for fifteen seconds with its tip still in contact with the glass. The receiving vessel is then removed, leaving in the jet of the pipette the liquid that is still there.

Standardisation.—Find the weight of an empty weighing-bottle or a small flask, which need not be dried inside. Fill the pipette to the mark with distilled water, run the contents into the weighing-bottle, and reweigh. Find the temperature of the water and, with the help of the table on p. 45, calculate the volume of the observed weight of water. If the error is greater than the permissible error (see p. 52), the pipette must be corrected in the following manner.

A rough estimate as to how far to place the new mark from the old graduation may be obtained by noting how far the water sinks in the narrow tube when one drop is run out of

[1] Unless the tip of the forefinger that is placed on the upper end of a pipette is smooth and *slightly* moist, it may be found impossible to manipulate the instrument with ease and certainty. If the finger-tip is rough, rub it with pumice; and, immediately before using a pipette, moisten the finger-tip with the lips or tongue and rub the finger and thumb together for a moment.

the pipette. One drop of water weighs, roughly, about 0·05 gram. Gum a strip of paper along the pipette and make a mark where it is thought the graduation should be.

Weigh the amount delivered by the pipette with this new graduation, and calculate the volume to which this corresponds. If this is not quite correct, it will serve as a guide to the exact position. When it is certain (by a repetition of the weighing) that a mark on the paper is the correct position for the graduation, a line should be etched on the glass at this place (see p. 49). Before removing the paper with the graduation mark, wash off the etching solution and examine a small portion of the line to be sure that it is properly etched.

The N.P.L. regulations require that, for the two classes of pipettes, the following tolerances must not be exceeded [1] :—

Capacity ml. . .	2	5	10	20	25	30	50	100	250
Tolerance ± ml. . .									
Class A . . .	0·01	0·02	0·02	0·02	0·03	0·03	0·04	0·06	0·10
Class B . . .	0·02	0·03	0·04	0·05	0·06	0·06	0·08	0·12	0·2

Standardised pipettes are now usually marked thus :—

50 ml.
D. 20° C.
(30+15) sec.

D. denotes delivery (and not content), thirty seconds is the time of outflow, and fifteen seconds the additional time to be allowed for drainage.

Graduated Pipettes.—Some pipettes, instead of being marked to deliver one specified volume of liquid, have a series of graduations like a burette, and are very useful for rapidly measuring out odd amounts of liquid. They cannot, however, be used with the same precision as the ordinary type of pipette.

USE OF A BURETTE

A burette is a measuring instrument of lower precision than a pipette or graduated flask, and great care is necessary to secure the best results. Precision in carrying out titrations may be improved by slightly greasing the tip by drawing the fingers over it, or by dipping the warmed burette-tip into

[1] N.P.L. pamphlet, *Tests on Volumetric Glassware.*

melted wax, and shaking off any excess. With a fine jet, drops as small as 0·02 ml. may then be obtained.

A burette is usually graduated in tenths of a millilitre. It is fitted at the lower end with a glass tap or with a rubber tube and clip, so that the flow of liquid may be regulated and stopped as desired (Fig. 23). A glass tap must be used with potassium permanganate and iodine solutions, since these attack rubber. In order that the measurements with a burette may be accurate, attention must be paid to the following points :—

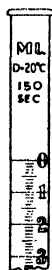
FIG. 23.

(1) The burette must be clean (see p. 47).

(2) The tap must be lubricated with a mere trace of a suitable lubricant. (Vaseline, or a mixture made by melting one part of *black* rubber with six parts of vaseline will be found satisfactory.) The tap must not leak.

(3) The burette must be clamped *vertically*, and at a convenient height above the bench. As a rule, it is best to adjust the burette so that the tip of the jet is about half an inch above the top of the receiving vessel.

(4) The rate of discharge is a very important consideration in the use of a burette, and is dealt with more fully on p. 56. The time taken in delivering the liquid from a 50 ml. burette should be about 150 seconds. In a good burette the jet is of such a size that the proper rate of delivery cannot be exceeded.

(5) The level of the liquid in a burette is read by noting the graduation opposite the lower boundary of the dark portion of the meniscus (except with opaque solutions as explained on p. 102), and an accurate reading requires (*a*) suitable illumination of the meniscus, (*b*) avoidance of parallax error. A simple method of illuminating the meniscus is to hold a white card behind the burette, as shown at M in Fig. 24. The eye must be at the same level as the

meniscus; it is evident that readings from positions A or B will be incorrect.

A more satisfactory device, which gives good meniscus illumination and completely eliminates parallax error, is shown in Fig. 25.[1] A piece of

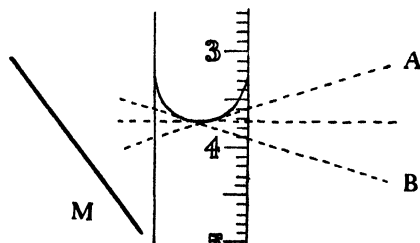



FIG. 24.

white celluloid, measuring about 7 cm. by 4 cm., has two-thirds of its area blackened, as shown in diagram A; exactly covering the black area and fixed to it by means of two eyelets is a strip of transparent celluloid. The device is slipped over the burette (as shown in diagram C) and will remain in any desired position. A burette reading is made as follows:—

The device is placed on the burette so that the upper margin of the black area is just below the meniscus. (The meniscus then appears as a black crescent with a very sharp lower outline.) The eye is brought into such a position that the upper edge of the transparent celluloid (in front of the burette) and the upper margin of the black area (behind the burette) are seen as one coincident line, and the device is gradually raised until this line forms a tangent to the black crescent of the meniscus. This is shown in diagram B and also at F. The slightest movement of the eye throws the front and back margins of the device out of alignment, while the slightest movement of the device itself causes the meniscus to appear above or below the coincident margins, as shown at D and E. After adjusting

[1] This device may be obtained from Mr A. H. Baird, Lothian Street, Edinburgh.

the device in this manner, the burette reading is obtained, without further reference to the meniscus, by noting the position on the burette of the upper margin of the transparent celluloid. It is possible

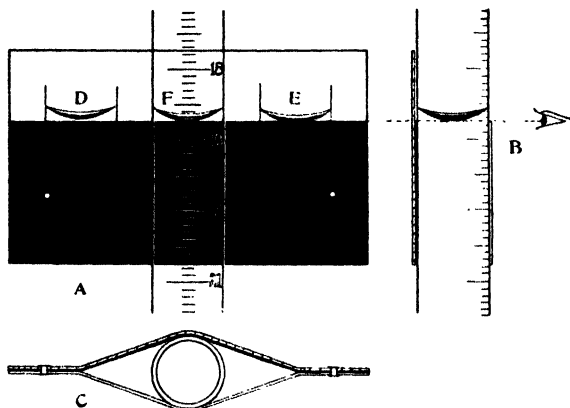



FIG. 25.

to read to the nearest 0·01 ml., especially with the aid of a pocket lens.

Another device is found in the Schellbach burette (Fig. 26) which has a broad, white band along the back and a narrow (usually blue) band in the middle of the white one. The error due to parallax is lessened, but is not completely eliminated by this device.

FIG. 26.

When washing out a burette, the open end should be closed with a cork—not with the finger, because this makes the glass greasy; or the burette may be washed by running in some water and tilting the tube up and down. The tap must not be opened while the burette is inverted, or grease will be introduced from the tap. After washing a burette it should be drained as completely as possible, and, before filling it with a solution, it must be rinsed twice with a little of the solution in order to remove the water still adhering to the wall. The solution should be poured into the burette through a small, dry funnel. The funnel must be removed from the burette and the air expelled from the jet before the initial reading is taken.

In titration it is often possible to judge the end-point with a precision of about 0·01 ml. To enable this to be done and to avoid overstepping the end-point, the solution in the burette must be cautiously added in fractions of a drop at a time, when near the end-point. Fractional drops may be removed from the jet of the burette with a stirring-rod, or by bringing the side of the receiving vessel into contact with the jet.

Calibration of a Burette

A burette that is to be used for accurate work must be tested or calibrated, unless it is a verified instrument. The calibration of a burette demands very careful manipulation on the part of the operator, who must have had previous experience in handling such instruments and must know how to use them properly.

It has been definitely established that practically no after-drainage takes place in a burette, if the rate of outflow is not greater than a certain speed. If this speed is exceeded owing to the delivery jet being too large, considerable drainage takes place for several minutes. For burettes accepted for testing by the National Physical Laboratory, the time of outflow must be between certain limits according to the length of stem graduated, this length in any case not exceeding 70 cm.

These limits are given in the following table[1] :—

Graduated length in centimetres	25	30	35	40	45	50	55	60	65	70
Minimum time of outflow in seconds :										
Class A	50	60	70	80	90	100	110	120	130	140
Class B	35	40	50	55	60	70	75	80	90	95
Maximum time of outflow in seconds :										
Classes A and B	90	105	120	135	150	165	180	195	210	225

The time of outflow is taken with the tap fully open, and the jet *not* in contact with the inside of the receiving vessel.

Procedure.—Clean the burette very carefully. Lubricate the tap and make sure that it does not leak. Clamp the burette *vertically* at a convenient height above the bench. Fill the burette with distilled water, the temperature of which is the same as that of the room. Record this temperature. Expel

[1] N.P.L. pamphlet, *Tests on Volumetric Glassware.*

air from the jet of the burette. With the help of the device shown in Fig. 25, carefully adjust the level of the water to the zero graduation of the burette. Remove any drop adhering to the jet by bringing the jet into contact with the side of a beaker.

Water is then run out into a flask which has been weighed to the nearest centigram with the tap *fully* opened until the meniscus of the water is within 1 cm. of the point under test. The speed is then slackened to enable the meniscus to be brought exactly on to the mark. No period of draining should be allowed. Remove any drop adhering to the jet by bringing the inside of the receiving flask into contact with the jet. This procedure is carried out for each of the marks to be tested, say 5, 10, 15, 20, etc. The zero mark is always taken as the starting point, as a very small drainage might take place between readings, and impair the accuracy of the intermediate determinations. Repeat the whole process and tabulate the results in four columns: (1) Burette reading, (2) Mean of observed weights of water delivered, (3) True volume at 20° calculated from the data on p. 45, (4) Correction at each mark.

Care must be taken to avoid mistakes in the sign (plus or minus) of the corrections. A plus correction must be added to, and a minus correction must be subtracted from, the corresponding burette reading in order to obtain the true volume. By plotting the corrections against the corresponding burette readings, a curve of corrections is obtained. Since the error in reading a burette is about 0·01 ml., the corrections themselves may involve an equal error, and a "smoothed" curve may therefore be drawn through the points. The correction at any burette reading may be obtained at once from the curve.

It is advisable to reject a burette if there are serious errors, and particularly if there are marked irregularities in it.

The tolerances allowed on burettes[1] are:—

Total capacity ml.	2	5	10	30	50	100	200
Maximum error allowed at any point tested, and also maximum difference allowed between the errors at any two points tested							
Class A ± ml.	0·01	0·02	0·02	0·03	0·06	0·1	0·2
Class B ± ml.	0·02	0·03	0·04	0·06	0·1	0·2	0·4

[1] N.P.L. pamphlet, *Tests on Volumetric Glassware*.

For example, in the case of a 50 ml. burette Class A, an error of +0·04 ml. at one point must not be accompanied by an error of −0·03 ml. at another point.

For accurate work it is advisable to calibrate a burette at every millilitre mark, as experience shows that considerable variations are liable to occur with even these small differences of volume.

GENERAL NOTES ON THE PREPARATION OF STANDARD SOLUTIONS

For obvious reasons it is desirable that a standard solution should not alter in concentration on keeping; volatile or unstable substances are therefore to be avoided if possible.

Solutions more concentrated than *normal* are rarely required in analytical work. More dilute solutions may be prepared with accuracy from a standard N solution by using a *standardised* pipette and flask.

As a general rule, the solution or solid (finely powdered before weighing) from which the standard solution is to be prepared is washed into the standard flask through a funnel with a wide stem. The flask must of course be clean, but it is unnecessary to dry it. Standard flasks should not be heated. If it is necessary to apply heat in the preparation of the solution, this operation should be performed in a beaker, and the solution then cooled before pouring it into the flask. If the solution is prepared in a beaker or other vessel, the volume of liquid must be such that ample wash-water may subsequently be used without exceeding the volume of the standard flask.

Before making up to the mark, the contents of the flask must be sufficiently mixed, to ensure that there is no considerable difference in concentration between the top and bottom layers. To accomplish this, the contents of the flask are mixed by rotation when the level is a little below the neck. If this is not done, an error is introduced by the change of volume that occurs when mixing takes place.

The solution should be at or near 20° before making it up to the graduation mark.[1] Attention to this is specially necessary if the process of solution or dilution is accompanied by a

[1] The error introduced is approximately 1 part in 1000 when the temperature is 5° higher, and the solution is being made with a weighed amount of substance.

considerable heat evolution, *e.g.* with sulphuric acid or sodium hydroxide. In that case it is advisable to dilute almost to the full amount and cool by running tap-water over the flask. The final addition of water to bring the level up to the graduation mark is most easily made from a wash-bottle with a fine jet.

Before pouring any of the liquid out of the flask, the stopper should be firmly inserted and the contents thoroughly mixed by inverting the flask and shaking at least ten times. This must on no account be neglected, otherwise serious errors will be introduced.

The solution is best stored in a stoppered bottle. The bottle must be rinsed out two or three times with small quantities of the solution, the portions used for rinsing being rejected. The bottle should be clearly labelled with the name of the solution, the exact concentration, and the date of standardisation. If there is more than one common method for the

Hydrochloric Acid 1·017N (by calcspar) 29/3/42

standardisation of the solution, the label should indicate which method was adopted.

When a bottle of standard solution has been set aside for some time, drops of liquid will be found to have condensed on the upper part of the bottle. As these drops differ in concentration from the main portion of the solution it is always advisable to shake the bottle before use. If any sediment is present, this should be allowed to settle after shaking.

Preparation of a Standard Solution of a desired Concentration

The usual practice in the preparation of a standard solution is to make the solution of approximately the required concentration, then to determine the exact value, and use this value as a " factor " in the calculations. It is sometimes necessary, however, to prepare a solution which is, for example, *exactly* normal, or decinormal, and the following is an illustration of a method that may be used.

Preparation of an exactly Normal Solution.—In preparing the solution it is better to make it somewhat too concentrated at first rather than too dilute, as it is an easier matter to alter the concentration by addition of water than by addition of weighed quantities of the solute.

Example.—A solution of sodium carbonate was found by titration to be 1·045N. It is clear that 1000 ml. of the solution contains 1·045 equivalents, and that it could be made exactly normal by increasing the volume to 1045 ml. If 45 ml. of water were added to 1 litre of the solution, there would then be 1·045 equivalents in *about* 1045 ml.[1]

The approximate volume of the solution is determined by means of a measuring cylinder. Suppose, for example, the volume of the sodium carbonate solution was found to be 440 ml. The amount of water to be added is then

$$\frac{440}{1000} \times 45 = 19{\cdot}8 \text{ ml.}$$

The 19·8 ml. of water is run out from a burette into the solution in the measuring cylinder. (Take care to add too little rather than too much water.) The solution is poured back into the bottle, shaken, and again titrated with standard acid. If it is still too concentrated, again add the calculated amount of water and again titrate. After the second adjustment the solution should be of the required concentration ; if not, continue the process. After adding any water, always return the solution to the bottle and shake it before titrating it with the acid.

Use of a Standard Solution of Arbitrary Strength

In commercial analyses, where many similar determinations of the same constituent are to be made, standard solutions are often prepared of such a strength that the number of millilitres required in a titration indicates without further calculation the required proportion of the constituent present. *E.g.* see p. 456, where, in the determination of chlorine in water, a standard solution of silver nitrate containing 4·79 grams per litre is used, 1 ml. of which corresponds to 1 mgrm. of chlorine.

[1] Addition of 45 ml. of water will not give exactly 1045 ml. The volume obtained when a solution is diluted with water is slightly less than the sum of the volumes taken, but the difference is so small that it may be neglected except with concentrated solutions.

CALCULATIONS IN VOLUMETRIC ANALYSIS

When a solution whose strength has to be determined has been titrated against a known standard solution, the weight of substance in the former, or the weight per litre as may be desired, can then be calculated, by means of the chemical equation for the reaction employed, from the known weight of reagent in the volume of the standard required. This method has been adopted in this book.

It is usual in practice, however, to mark standard solutions with their normality only, and in this case a more rapid calculation may often be made by means of the equation

$$N_1V_1 = N_2V_2,$$

where N_1 and V_1 are the normality and volume of one solution taken, and N_2 and V_2 the normality and equivalent volume of the other. From the normality of the unknown solution thus found, the grams per litre of the required constituent can then be calculated from its equivalent weight for the reaction employed.

The relation $N_1V_1 = N_2V_2$ is also useful in making up standard solutions from more concentrated ones: *e.g.* if 250 ml. of a 0·015N solution is to be prepared from a 0·95N solution, the volume of the latter to be made up in a graduated flask will be $\frac{250 \times 0{\cdot}015}{0{\cdot}95}$ ml.

When a known weight, W grams, of a substance is used in an indefinite volume, V ml., of liquid, the normality of this solution, N, will be $\frac{1000W}{EV}$, and NV will be $\frac{1000W}{E}$, E being the equivalent weight for the reaction of the substance whose weight only is known.

Acidimetry and Alkalimetry

THE determination of the concentration of acids by means of standard alkali solutions is known as acidimetry, and the reverse process as alkalimetry. The choice of acids and alkalis for standard solutions is partly a matter of convenience, but for certain purposes the choice is restricted, *e.g.* a standard sodium carbonate solution cannot be used instead of a standard sodium hydroxide solution for the determination of a weak acid such as acetic acid.

Standard Acids.—The only acids in common use are hydrochloric and sulphuric acids. The preparation of normal solutions of each, with various methods of standardisation, will be found below; more dilute standard solutions are best prepared by dilution of the normal solution.

Standard Alkalis.—Sodium hydroxide, sodium carbonate, and barium hydroxide are all used for standard solutions, and each has advantages over the others for special purposes. The selection of an indicator is of special importance in connection with standard alkalis; and it is essential that in standardising and in subsequently using a standard alkali one and the same indicator should be used.

NOTES ON THE USE OF INDICATORS

The indicators used in acidimetry and alkalimetry are sometimes said to show when a solution is neutral, but this is only approximately true.

A neutral solution is one in which, as in ideally pure water, the concentrations of the acid ion (hydrion) $H^{\cdot}$ and the alkaline ion (hydroxidion) OH' are equal, and are each approximately 1×10^{-7} normal (0·0000001 N). If the concentration of hydrion is greater than that of hydroxidion, the solution is acid; if it is less than that of hydroxidion, the solution is alkaline. In pure water and in all dilute aqueous solutions, whether acid, neutral, or alkaline, the product of the concentrations of hydrion and

hydroxidion is constant and approximately 1×10^{-14}. Accordingly, if the hydrion concentration is, for example, 10^{-5}N, the hydroxidion concentration is 10^{-9}N, and the solution is acid; and if the hydrion concentration is 10^{-8}N, the hydroxidion concentration is 10^{-6}N, and the solution is alkaline.

It is becoming customary to speak of all solutions, whether acid or alkaline, in terms of their hydrion concentration, and in order to avoid long decimals or negative indices, and to enable the whole range of acids and alkalis to be readily graphed, a logarithmic device is used. As the logarithm of the actual hydrion concentration would usually be negative, the logarithm of the reciprocal is taken, this being called the *p*H of the solution. If *c*H is the hydrion concentration in grams per litre,

$$pH = \log\left(\frac{1}{cH}\right).$$

For example, the hydrion concentration of decinormal hydrochloric acid is about 0·093 gram per litre. $1/cH = 10·7$, and $\log 10·7 = 1·03$. The *p*H of this acid solution is therefore 1·03. Similarly, the *p*H of decinormal sodium hydroxide solution, which has a hydrion concentration of about $1·175 \times 10^{-13}$ gram per litre, is 12·93. The *p*H of pure water is approximately 7.

The use of *p*H, though so convenient, tends to be misleading at first, and the following points should be noticed. Acid solutions have a *p*H less than 7, and alkaline solutions a *p*H greater than 7, the *p*H value increasing as the hydrion concentration falls. A unit change in *p*H means a tenfold change in hydrion concentration. The mean hydrion concentration between *p*H 2 and *p*H 3 is not represented by *p*H 2·5, but by *p*H 2·3.

Now the *p*H of a solution can be most accurately determined by an electrometric method (see p. 193), and if a series of readings of *p*H are taken as a strong (*i.e.* highly ionised) alkali is added to a strong acid, and these readings plotted, a curve of the type shown in Fig. 27 is obtained, in which there is seen to occur a large change in *p*H produced by a small addition of alkali at a certain point. The curve becomes almost parallel with the *p*H axis for some distance, and then bends away again. This region of abrupt change shows the

existence of a stoichiometric point. When acid and alkali are both strong, the portion of the curve parallel to the *p*H axis extends over a considerable range of *p*H ; but if either is weak, the parallel portion is shorter, and may not be readily discernible. Further, owing to the hydrolysis of the salt formed, this portion of the curve may not contain or pass through the point of exact neutrality, *p*H 7. If the alkali is weak, hydrolysis forms the non-ionised base, and the *p*H will be less than 7

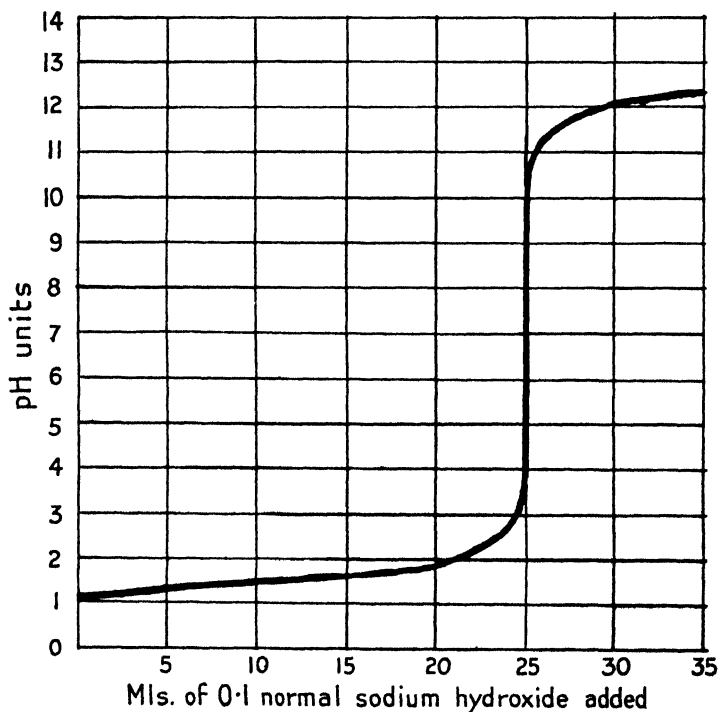



FIG. 27.

owing to the presence of excess of free hydrions ; while if the acid is weak, non-ionised acid will be formed, and the *p*H will be greater than 7. *It is therefore the p*H *of the solution of the salt formed* which is important as showing the presence of equivalent amounts of acid and alkali. The object of an indicator is to show in a rapid and convenient manner when this *p*H has been reached.

Indicators for acids and alkalis are usually organic compounds which exhibit a conspicuous change of colour when the

*p*H of a solution containing them passes over a certain range. This range differs in the case of different indicators, and as a rule does not include the point of absolute neutrality, *p*H 7. Methyl orange, for example, is red in solutions whose *p*H is less than about 3, and yellow in solutions whose *p*H is greater than about 4·4. Phenolphthalein is colourless at *p*H values less than 8, and pink at *p*H values greater than about 9.

It is essential, therefore, that the characteristic range of the indicator chosen for a titration must coincide with that part of the titration curve which is approximately parallel to the *p*H axis, and preferably it should actually contain the *p*H value of the salt which is formed when equivalent amounts of the acid and alkali used have been mixed. Since in the case of the titration of a strong acid by a strong alkali, the titration curve is approximately parallel to the *p*H axis over so wide a range as from 3·5 to 10·0, any indicator whose characteristic range occurred within these limits might be used. Phenolphthalein, however, would show the end-point slightly after the stoichiometric point, while methyl orange would show it slightly before, because these indicators have ranges situated near the limits of this critical portion of the curve. The most accurate result would be obtained with an otherwise suitable indicator, whose characteristic range actually included the *p*H of the salt solution formed at the stoichiometric point—in this case about *p*H 7; *e.g.* bromo-thymol blue (*p*H range 6-7·6).

It follows from the above considerations that methyl orange would be valueless for the titration of a weak acid, and phenolphthalein for that of a weak base, because in each case the change in colour of the indicator occurs over a range which does not even coincide with the critical part of the titration curve.

The titration of a weak alkali by a weak acid cannot be carried out satisfactorily with any indicator, as the amount of change of *p*H for a small addition of acid near the stoichiometric point is too small to cause a sufficiently sharp colour change in the indicator, even though the range of the latter covers the *p*H of the salt formed at the stoichiometric point.

Owing to the fact that the *p*H range of colour change of methyl orange occurs at a *p*H less than 5, this indicator is not affected by very weak acids such as carbonic acid, boric acid, etc. It is therefore possible to titrate carbonates, borates, etc., of strong bases by means of a strong acid in the presence of

methyl orange, as if the strong base alone were present. Sodium borate, for example, acts in such circumstances as if its base were in the form of sodium hydroxide. If, on the other hand, it is desired to estimate sodium hydroxide in the presence of sodium acetate by titration with a strong acid, phenolphthalein must be used, as the use of methyl orange would result in the approximate determination of the total soda.

Conversely, in the estimation of a strong acid such as hydrochloric acid by titration with a strong base in the presence of the salt of a weak base and a strong acid, such as ammonium chloride, it would be necessary to use an indicator such as methyl orange or methyl red, the colour change of which occurs before the *p*H has risen to the point of formation of the weak base.

There is available nowadays a large number of indicators covering the whole *p*H range from 1 to 14. Many of these are unsuitable for ordinary titrations, as their colour change is more or less affected by the presence of salts in solution. Those most satisfactory in general use are described below. The characteristics of others used in special cases will be given as the occasion arises.

Methyl Orange. *p*H range, 3·1 (red) 4·4 (yellow).—Very weak acids have little or no effect on this indicator and it is therefore specially adapted for the titration, with strong acids, of salts of very weak acids such as carbonates, bicarbonates, sulphides, silicates, borates, and arsenites. As carbonic acid is not entirely without influence on methyl orange, it is advisable in the titration of carbonates to expel most of the carbon dioxide when near the neutral point by warming and shaking the solution; the solution must be cooled before completing the titration, as the titration of hot solutions gives somewhat inaccurate results when using methyl orange.

Methyl orange cannot be used for the titration of weak acids. It may be used for ammonia, but methyl red gives a much sharper end-point. Its colour change is not so sharp with sulphuric acid as with other strong acids.

Methyl Yellow. *p*H range, 2·9 (red) to 4·0 (yellow).—This indicator is also very slightly affected by weak acids such as carbonic acid, and since it gives a more easily recognisable colour change than methyl orange it is preferable to the latter for the titration of sodium carbonate by strong acids.

Bromo-phenol Blue. *p*H range, 2·8 (yellow) to 4·6 (blue). —This indicator may be used instead of methyl orange, and is preferable to the latter in artificial light. The colour change passes through a pale green.

Methyl Red. *p*H range, 4·4 (red) to 6·2 (yellow).—This is the best indicator for the titration of ammonia or for solutions containing ammonium salts. It is more sensitive and gives a much sharper end-point than methyl orange with very dilute solutions of strong acids and alkalis. It is useless for weak acids like acetic acid. It may be used for the titration of soluble carbonates if the solution is heated to the boiling-point. Methyl red is, however, much less sensitive to carbonic acid than litmus or phenolphthalein, and the amount of carbonate present in an ordinary solution of sodium hydroxide is almost without influence on the indicator.

Bromo-thymol Blue. *p*H range, 6·0 (yellow) to 7·6 (blue). —This is an indicator whose *p*H range covers the true neutral point. The colour change is sharp. It may be used for the mutual titration of strong acids and strong bases.

Phenolphthalein. *p*H range, 8·2 (colourless) to 10 (red). —This indicator should be used only with strong alkalis free from carbonate. It is chiefly valuable for the titration of weak acids. Organic acids insoluble in water can be titrated in aqueous alcohol solutions with this indicator. Phenolphthalein must not be used for ammonia or in presence of ammonium salts. With carbonates of the alkalis it indicates " neutrality " roughly at the stage of bicarbonate.

Litmus. *p*H range, approximately 5·0 (red) to 8·0 (blue).— This indicator is rarely used in solution, owing to its variable composition and behaviour; but in the form of litmus-paper, it provides a ready means of distinguishing between acids and alkalis.

Mixed Indicators.—A mixture of certain indicators is useful in special cases where a definite narrow *p*H range is required. An example of such a mixture is given on p. 88 in the titration of a mixture of carbonate and bicarbonate using thymol blue and cresol red.

Universal Indicators.—These are mixtures of indicators so selected as to cover a wide range of *p*H, showing several changes of colour. They are convenient for showing the approximate *p*H of a solution, but are not suitable for purposes of a titration, as the colour change is more or less gradual.

Achromatic Indicators.—By mixing a suitable dye with an indicator, a more readily detectable colour change can be produced, especially in artificial light. The effect of the added dye is to reduce that part of the visible spectrum which is transmitted by the indicator both in acid and alkaline solution, thus making a greater contrast in colour between the acid and alkaline solution. The dye should have a colour complementary to that of the indicator at the mid-point of its colour change, and the colour of the dye itself must not be affected by acids or alkalis. Such a mixture gives a grey colour at the transition point, and may be used in titrating turbid or very dilute solutions. For instance, by adding a blue dye, such as methylene blue, to a solution of methyl orange, the mixture in alkaline solution is green. This changes to grey and finally to magenta as the *p*H falls. The appearance of the grey colour is taken as the end-point of the titration.

In connection with the use of the above indicators, it should be noted that ordinary sodium hydroxide invariably contains some carbonate, and if a solution of sodium hydroxide is intended for use with more than one indicator, it should be standardised separately, using each indicator, and the appropriate value for the normality, corresponding to each indicator, used in subsequent work.

The following instructions summarise the points to be observed in the volumetric estimation of acids and alkalis :—

(1) For the titration of a strong acid with a strong alkali (free from carbonate) and *vice versa*, any of the common indicators may be used if the concentration of the standard solution is not less than fifth-normal. With more dilute solutions use methyl red, bromothymol blue or phenolphthalein.

(2) For the titration of a weak acid with a strong alkali use phenolphthalein.

(3) For the titration of a weak alkali with a strong acid use methyl red, methyl orange or bromo-phenol blue.

(4) For the titration of salts of very weak acids with strong acids use methyl orange or methyl yellow (or in artificial light bromo-phenol blue). Methyl red or bromo-thymol blue may be used for carbonates or sulphides if the titration is carried out at the boiling-point of the solution.

(5) For the titration of a strong alkali with a strong acid in the presence of a salt of a strong base and a weak acid, use phenolphthalein.

(6) For the titration of a strong acid with a strong alkali in the presence of a salt of a strong acid and a weak base, use methyl orange or methyl yellow.

The titration of a weak acid with a weak alkali, *e.g.* acetic acid with ammonia, is avoided in practice, because no single indicator used in the ordinary way will give a sharp end-point; and it is not possible to titrate salts of very weak acids with weak acids, *e.g.* sodium carbonate with acetic acid.

For most titrations conical flasks with wide mouths are suitable, or, better still, conical beakers. They should be of resistance glass, as appreciable amounts of alkali are dissolved from ordinary glass, especially by boiling solutions.

The colour change of an indicator is best seen by having a white base (opaque white glass or paper) under the vessel, which should be placed near a window, though not in direct sunlight.

When the colour change at the end-point is not sharp, as when the solutions are very dilute, it is advisable to prepare a solution for comparison, containing approximately the same concentration of constituents and of indicator as will be present at the end-point of the titration. This solution should be placed beside that which is being titrated, so that the desired tint may be exactly matched, or the slightest difference observed.

Amount of Indicator to be Used

The preparation of indicator solutions is described in the Appendix (p. 477). It is important to note that *they are much more dilute than the solutions usually recommended.* It is a common mistake to use too much indicator, and if only *one* drop of a concentrated solution is required, the addition of "a few drops" represents a large excess. The concentrations recommended in the Appendix are so chosen that approximately 1 ml. of the indicator solution is required for each 50 ml. of liquid present at the end of the titration. One ml. of the indicator can be measured with sufficient

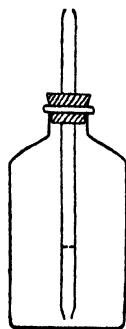



FIG. 28.

accuracy by means of a pipette (Fig. 28) roughly graduated to deliver this quantity.

Test Papers.—Books of paper are now available impregnated with a variety of common indicators as well as litmus. These enable the approximate *p*H of liquids to be determined, as well as merely showing whether they are acid or alkaline.

STANDARD HYDROCHLORIC ACID

(N solution contains 36·47 *grams HCl per litre)*

Standard hydrochloric acid may be obtained (1) by preparing a solution of approximately the desired concentration and then standardising it by one of the methods given below, or (2) by diluting a known volume or weight of "constant boiling-point" acid (see p. 75).

Commercial concentrated hydrochloric acid is usually about 11N. Prepare an approximately normal solution of the acid by diluting 90 ml. of the concentrated acid in a measuring cylinder to a litre. Transfer the solution to a bottle and *mix thoroughly* by inverting the bottle several times. Standardise the solution by the following methods:—(1) By means of calcspar; (2) by means of anhydrous sodium carbonate; (3) by means of borax; (4) by means of potassium iodate.

(1) Standardisation of Hydrochloric Acid by Means of Calcspar

A good specimen of calcspar may be regarded as pure calcium carbonate, except perhaps for work of more than ordinary accuracy. Select a good piece of this mineral weighing from 3 to 5 grams. Place it in a beaker and cover with dilute hydrochloric acid for two or three minutes to remove the fine powder on its surface. Wash the calcspar thoroughly with water and dry it with filter paper.

Clean and dry a small (100 ml.) beaker or conical flask. Place the piece of calcspar in the vessel and heat the vessel and contents in the steam-oven for one hour. Allow to cool in the balance-room for half an hour, and then find the weight of the vessel plus calcspar. With a pipette measure into the beaker or flask 25 ml. of the acid to be standardised. If a beaker is used, cover it immediately with a watch-glass; if a

flask is used, place a bulb in the mouth (Fig. 10, p. 27). Set aside for several hours or overnight.

Wash down the sides and cover of the vessel, add 1 ml. of methyl orange, and warm on the steam-bath until the solution becomes neutral (yellow colour).

Pour off the calcium chloride solution, and wash thoroughly by decantation, care being taken that there is no loss of any small pieces of the spar that may have become detached from the main portion. Drain off as much of the water as possible and dry the vessel and contents (with the cover removed) in the steam-oven for one hour. Cool in the balance-room for half an hour, and weigh.

From the loss of weight, calculate the concentration of the hydrochloric acid.

Example :—

Original weight of beaker and spar	=	16·5124 grams
Final ,, ,, ,,	=	15·2514 ,,
Weight of $CaCO_3$ dissolved by 25 ml.	=	1·2610 ,,

Therefore 1000 ml. of the acid will dissolve 50·44 grams $CaCO_3$.
But 1000 ml. of normal acid will dissolve 50·04 grams $CaCO_3$.

Therefore the given acid is $\frac{50{\cdot}44}{50{\cdot}04} = 1{\cdot}008$ normal.

Note.—The solubility of ordinary glass in water and in acid and alkaline solutions occasions an appreciable error in this and similar experiments in acidimetry. The error is considerable in the case of glass that has not been in use for some time. To minimise the error, the flask or beaker used in the above experiment should be "steamed," *i.e.* steam should be blown through it for ten minutes before finally rinsing it out for use. With resistance-glass vessels the error is practically negligible.

Alternative Method.—Weigh out accurately not more than 1 gram of powdered calcspar on a watch-glass. Wash this carefully by means of a wash-bottle into a small conical flask, using a funnel in the neck of the flask. Lift the funnel and run in from a pipette 25 ml. of the hydrochloric acid, at once replacing the funnel to guard against loss during the effervescence. After a few minutes warm the solution *gently* to complete the reaction and to expel most of the carbon dioxide.

Remove the funnel, washing both inside and outside into the flask, and wash down the inside of the flask.

Titrate the excess acid with an alkali solution, using 1 ml. of methyl orange as indicator. It is not necessary to know the concentration of this alkali, but its titration value against the acid must be known. The amount of unused acid is then calculated. Subtraction of this from the 25 ml. taken gives the volume neutralised by the calcspar, and from this the concentration of the acid is calculated.

Example.—0·9820 gram of calcspar were dissolved in 25 ml. of hydrochloric acid solution and 6·02 ml. of alkali were used in the "back titration," using methyl orange as indicator. Twenty-five ml. of this alkali, using the same indicator, neutralised 23·94 ml. of the acid. The 6·02 ml. of alkali correspond, therefore, to $\left(\frac{23 \cdot 94}{25} \times 6 \cdot 02\right)$ ml. $= 5 \cdot 76$ ml. of acid.

Therefore 0·9820 grams of $CaCO_3$ neutralised $(25 - 5 \cdot 76)$ $= 19 \cdot 24$ ml. of acid. The hydrochloric acid is 1·020 N.

(2) Standardisation of Hydrochloric Acid by Means of Anhydrous Sodium Carbonate

The sodium carbonate required for this purpose must answer the following tests :—

(1) Dissolve 1 gram in 25 ml. of distilled water; the solution should be perfectly clear. Add dilute nitric acid (free from chloride) in slight excess and then a few drops of silver nitrate solution. No turbidity (or only a *very faint* opalescence) should appear.

(2) Dissolve 1 gram in 25 ml. of distilled water. Add sufficient dilute hydrochloric acid (about 10 ml.) to make the solution *faintly* acid. Then add about 1 ml. of barium chloride solution, heat until boiling, and set aside until cold. No trace of barium sulphate should be precipitated.

If the sodium carbonate is free from chloride and sulphate and from insoluble impurities, it must next be dried. Heat 3 to 4 grams in a small porcelain basin (a platinum crucible is preferable) over a moderate Bunsen flame, with frequent stirring, for twenty minutes; regulate the flame so that the bottom of the crucible is barely red hot; the substance must

not fuse or form into hard lumps. Allow to cool partially, and transfer while still warm to a clean, dry weighing-bottle, dry sodium carbonate being very hygroscopic.

In order to avoid over-heating the carbonate, the basin or crucible may be heated on a sand-bath to 300° for thirty minutes, with frequent stirring.

When the weighing-bottle is perfectly cold, weigh it accurately, shake out from 1 to 1·3 gram of the carbonate into a suitable beaker or conical flask, and weigh again. Shake out a second quantity into another beaker, and again weigh.

Dissolve each portion of carbonate in about 30 ml. of water, add 1 ml. of methyl orange or, better, methyl yellow, and titrate with the hydrochloric acid. Calculate the concentration of the acid as follows :—

1·251 gram Na_2CO_3 required 23·52 ml. acid. Therefore 1 litre of acid is equivalent to $\frac{1\cdot251 \times 1000}{23\cdot52} = 53\cdot17$ grams Na_2CO_3. But 1 litre of normal acid is equivalent to 53·0 grams Na_2CO_3. Therefore the acid is $\frac{53\cdot17}{53\cdot0} = 1\cdot003$ N.

The two results should agree to about 2 in 1000.

Sodium bicarbonate, free from chloride and sulphate and insoluble impurities, may be used for the preparation of the normal carbonate. For this purpose, water and carbon dioxide are driven off by heating to a moderate temperature, as in the case of sodium carbonate, in a platinum crucible (or a porcelain basin) for thirty minutes, with frequent stirring.

Still more accurate results can be obtained by using pure dry sodium oxalate as the source of sodium carbonate. The former, being sparingly soluble, can be easily purified, and having no water of crystallisation, can be dried by heating to 130° C. After weighing a suitable quantity, it is ignited preferably in a platinum crucible just below the melting-point until the carbon that separates is burnt off. It is thus converted into its equivalent of sodium carbonate.[1] The platinum crucible should be supported in a hole cut in a sheet of asbestos in order to avoid combination with sulphur dioxide from coal-

[1] This method is of interest as it enables solutions of acids and alkalis to be linked up with those of potassium permanganate, sodium thiosulphate, etc., through the same standard.

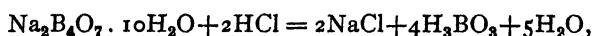
gas. If a porcelain crucible is used, it is not possible to burn off all the carbon without some of the sodium carbonate reacting with the glaze. The bottom of the crucible should be kept at not more than a low red heat for about half an hour, and after cooling the contents should be extracted with water and the solution filtered. After washing thoroughly, the filter should be burnt and the ash extracted with water, adding this extract to the main solution.

(3) Standardisation of Hydrochloric Acid by means of Borax

In spite of the fact that borax contains water of crystallisation, it has much to recommend it as a standard in acidimetry. It has a high equivalent weight, and the boric acid liberated after neutralisation by a strong acid is so weak that it has no effect on an indicator such as methyl orange, or even methyl red. Further, as it is sparingly soluble in cold water, it can easily be purified by recrystallisation.

Recrystallise a sample of borax by dissolving 15 grams in 50 ml. of hot water. This proportion avoids the formation of crystals above 55° on cooling, and thus prevents the formation of any pentahydrate. Filter the hot solution, and cool the filtrate rapidly. Filter, and free the crystals from mother-liquor by suction. Wash twice with cold water, and then four times with 5 ml. portions of acetone (or with two 5 ml. portions of 95 per cent. alcohol followed by two 5 ml. portions of ether). Spread the crystals in a thin layer on a clock-glass, and allow them to stand at room temperature overnight. Borax is not hygroscopic, but at a temperature slightly over 20° very slowly loses water of crystallisation if the humidity of the air is low. It should therefore be kept in a well-stoppered bottle after the above treatment.

Borax reacts with hydrochloric acid according to the following equation :—

$$Na_2B_4O_7 . 10H_2O + 2HCl = 2NaCl + 4H_3BO_3 + 5H_2O,$$

so that the equivalent weight of borax is $\frac{381 \cdot 4}{2}$, *i.e.* 190·7.

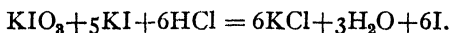
For the standardisation of approximately normal hydrochloric acid, about 4 grams of borax are weighed accurately into a conical flask or beaker, and 100 to 150 ml. of hot distilled

water and 1 ml. of methyl orange or methyl red are added. The acid is run in from a burette, the solution being cooled before the end-point is reached.

If the hydrochloric acid is approximately N/10, methyl red is a more satisfactory indicator than methyl orange. A solution for comparison should be placed alongside (p. 69). For greater accuracy, especially when using methyl red, the solution should be boiled after the indicator just shows a red tint in order to remove small amounts of dissolved carbon dioxide. A further drop or two of acid will then be required to finish the titration.

(4) Standardisation of Hydrochloric Acid by means of Potassium Iodate

Potassium iodate is a reliable substance for use in the standardisation of acids. A known weight of the iodate is added to a solution containing excess both of potassium iodide and of sodium thiosulphate. The subsequent addition of the acid to be standardised liberates its equivalent of iodine according to the following equation :—

$$KIO_3+5KI+6HCl = 6KCl+3H_2O+6I.$$

The free iodine reacts with the excess of thiosulphate present. As soon as the iodate is completely reduced, the *p*H of the solution falls sharply, and this can be detected by methyl red, which is added at the commencement of the titration.

Preparation of Standard Hydrochloric Acid Solution from the Constant Boiling-Point Acid

Standard hydrochloric acid can be prepared directly by distillation, followed by dilution to the required strength. This method depends on the fact that by distilling hydrochloric acid of any strength, the boiling-point rises and eventually reaches a maximum value. After this point is reached the distillate has a constant concentration of 20·24 grams of hydrochloric acid in 100 grams of liquid, if the distillation has been carried out at ordinary atmospheric pressures.

The density of the constant boiling-point acid distilled at 760 mm. is 1·096 at 25° C. It is advisable therefore to start

with acid of approximately this density by placing 540 ml. of concentrated hydrochloric acid and 420 ml. of water in a distilling flask (or retort) attached to a condenser. The diluted acid is distilled and the first 650 ml. of the distillate is collected for ordinary use, and if the boiling-point has become constant, the next 200 ml. of the constant boiling-point acid is collected in a separate receiver.

For very accurate work the distillation should be carried out in apparatus made of Pyrex glass, and back pressure must be eliminated as far as possible by avoiding any constriction in the flow of vapour, *e.g.* the bore of the condenser, etc., should not be less than 6 mm. The rate of distillation should be from 8 to 10 ml. per minute and the distillation must be continuous from the beginning to the end. About 75 per cent. of the acid should pass over before collecting the constant boiling-point fraction which should consist of the next 10 to 15 per cent. At least 100 ml. should be left in the distilling flask at the end, and the upper part of the flask must be protected from superheating by supporting the flask on asbestos board with a hole cut in it. The barometric pressure must be read at the beginning and end of the distillation.

The weight of the distillate collected at various atmospheric pressures, which on dilution to a litre will give a normal solution of hydrochloric acid, is shown in the following table :—

Atm. pressure in mm.	Grams. of C.B.P. acid containing one mol. of HCl.
770	180·39
760	180·17
750	179·96
740	179·75
730	179·53

In weighing out the required amount of liquid it is convenient to make the final adjustment by means of a capillary tube. If great accuracy is not required, instead of weighing the distillate, 164·2 ml. at 20° C. should be diluted to a litre to give a normal solution if the distillation was carried out at 760 mm. For other pressures 0·2 ml. must be added to or subtracted from this volume for each 10 mm. above or below 760 mm. respectively. The constant boiling-point acid is not hygroscopic or readily volatile, and in a well-stoppered resistance-glass bottle will remain constant in strength for long

periods. Although this method takes time it is one of the most accurate for obtaining standard hydrochloric acid.

STANDARD SULPHURIC ACID

(*N solution contains* 49·04 *grams* H_2SO_4 *per litre*)

Dilute 30 ml. of ordinary concentrated sulphuric acid by running it slowly into 150 to 200 ml. of cold water contained in a flask. (**Caution.**—The acid must be run into the water, not *vice versa.*) After cooling the solution under the tap, pour it into a measuring cylinder and dilute to a litre. The solution prepared in this way will be slightly above normal; the exact concentration must be found by standardisation.

Standardisation.—Sulphuric acid may be standardised in exactly the same manner as hydrochloric acid with weighed quantities of sodium carbonate (see p. 72).

Calcspar cannot be used as a standard for sulphuric acid on account of the insolubility of calcium sulphate.

Methyl orange does not give as sharp an end-point with sulphuric as with hydrochloric acid, methyl red being more satisfactory.

STANDARD SODIUM HYDROXIDE

(*N solution contains* 40·00 *grams* $NaOH$ *per litre*)

Sodium hydroxide is very deliquescent, and the commercial "sticks" contain varying amounts of carbonate. For most purposes, the solution made from ordinary "white sticks" may be used, but when a "carbonate-free" solution is required, it must be prepared by one of the special methods given below.

Weigh about 42 grams of sodium hydroxide on a rough balance. Drop the sticks without delay into a bottle containing about 800 ml. of water. Close the bottle with an ordinary cork or a rubber stopper, and shake gently during the process of solution, otherwise the heat evolved may cause the bottle to crack. Dilute the solution to about 1 litre. (A mark should have been made on the bottle to show this volume.) Allow the solution to cool before standardising it.

Preparation of Carbonate-free Sodium Hydroxide

Sodium hydroxide is often used for the determination of weak acids, with phenolphthalein as indicator. If any carbonate is present, the end-point is not satisfactory. Commercial sodium hydroxide almost invariably contains some carbonate as impurity, and a solution sufficiently free from carbonate for ordinary purposes may be prepared as follows :—Dissolve 200 grams of sodium hydroxide in 250 ml. of water contained in a conical flask. Transfer the solution to a tall, narrow Pyrex bottle with a rubber stopper fitted with a soda-lime tube, and set the bottle aside for a week or longer until the undissolved sodium carbonate has settled. The clear solution is practically free from carbonate, and is about 16·5N. To prepare an approximately normal solution, dilute 61 ml. to 1 litre with CO_2-free water.

When it is essential to have a solution almost entirely carbonate-free it is preferable to prepare a solution from metallic sodium. The following method may be used, except in the rare cases where the presence of alcohol is not permissible.

Cut away the layer of oxide from the surface of a piece of sodium, using alcohol to lubricate the knife. Weigh out approximately 23 grams of the metal and drop it, in small pieces at a time, into about 50 ml. of ethyl alcohol contained in a porcelain basin. When the reaction becomes sluggish, it can be hastened by the *cautious* addition of a few drops of water. During the reaction protect the solution from atmospheric carbon dioxide by means of a clock-glass over the basin ; and, immediately solution is complete, dilute with CO_2-free water (p. 83) to a litre.

This solution will be almost free from carbonate, but it will only remain so if it is carefully protected from atmospheric carbon dioxide. The apparatus described on p. 83 is convenient for that purpose.

A better, though longer method for preparing carbonate-free sodium hydroxide from sodium consists in first preparing sodium amalgam by electrolysis of a solution of ordinary sodium hydroxide and subsequent treatment of the amalgam with water free from carbon dioxide.

Fit a cork with three small holes in a 250 ml. round-bottom flask. Into one hole fit a glass tube, in which a short piece

of platinum wire is sealed, the tube being long enough to allow the platinum wire to reach the bottom of the flask. Add 30 ml. of mercury, which will cover the platinum wire, and connect the mercury to the negative pole of a six-volt accumulator capable of giving a current of about 2 amperes. The connection is made by adding a little mercury to the glass tube and inserting a copper wire. The second hole in the cork is fitted with a shorter piece of glass tube into which is sealed a short piece of platinum wire, the other end of the wire being welded to a piece of platinum foil about 1 square centimetre. This electrode is connected to the positive pole of the accumulator in a similar manner to the first. Now add about 120 ml. of approximately five-normal sodium hydroxide, and adjust the tube carrying the platinum foil so that the latter is just immersed in the sodium hydroxide solution, and well above the mercury surface. The current passing will be about 1·5 amperes, so that allowing for unavoidable losses the electrolysis should be continued for about two and a half hours to yield a tenth of an equivalent of sodium. It is not advisable to make the amalgam more concentrated than this as a considerable amount of solid would separate. Transfer the amalgam to an evaporating dish, agitate it several times with separate portions of distilled water, and dry it with filter paper.

To make up an approximately decinormal solution of sodium hydroxide, almost fill a Pyrex litre flask (not graduated) with distilled water and boil this gently for fifteen minutes. Allow this to cool after inserting a stopper with a soda-lime tube attached. When the water has cooled to about 60° add the whole of the amalgam prepared as described above, and replace the stopper with the soda-lime tube. The reaction may be allowed to proceed at the ordinary temperature, but the sodium only reacts slowly. It is therefore better to hasten the reaction by keeping the flask warm. The solution should then be rapidly transferred to the apparatus described on p. 83.

Standardisation of Sodium Hydroxide

The solution must always be standardised. If it is not carbonate-free, methyl orange is to be used as indicator, and the titration carried out with standard hydrochloric acid. In

the case of carbonate-free sodium hydroxide, phenolphthalein may also be used as the indicator, and instead of standard hydrochloric acid, one of the following organic compounds may be used with advantage :—

	M.-P.	Eq. Wt.	Solubility.
Succinic acid	187° C.	59·04	6·8 (20°) ; 121 (100°)
Benzoic acid	122° C.	122·12	0·3 (20°) ; 5·9 (100°)
Potassium hydrogen phthalate .	—	204·22	10·2 (25°) ; 36·1 (100°)

These are excellent standards, as they are anhydrous substances, and easily purified.

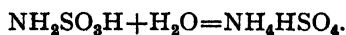
Oxalic acid and potassium tetroxalate are also used for standardising sodium hydroxide, but they are less reliable, and, being hydrated, their purity cannot be checked by melting-point determinations.

(1) Standardisation of Sodium Hydroxide by means of Standard Hydrochloric Acid

Titrate 25 ml. of the sodium hydroxide solution with standard hydrochloric acid, using as indicator (1) methyl orange, (2) bromo-thymol blue, and (3) phenolphthalein, and if the results are appreciably different, the value of the normality should be calculated separately for each indicator.

(2) Standardisation of Sodium Hydroxide by means of Sulphamic Acid (Aminosulphuric Acid)

Sulphamic acid has recently been recommended as a standard in alkalimetry. It is a white crystalline substance, made by the action of fuming sulphuric acid on urea. It is not hygroscopic and is stable in the solid form below 80°. In solution it is slowly hydrolysed to ammonium bisulphate.

$$NH_2SO_3H+H_2O=NH_4HSO_4.$$

Its solubility is about 18 grams in 100 grams of water at 15°. A dilute solution of the pure substance does not give a precipitate with barium chloride, but some commercial samples give a reaction for sulphate and may also contain urea.

Therefore unless the sample is known to be pure it must be recrystallised as follows :—

Heat 120 ml. of water to 75° in a 250 ml. conical flask, add 50 grams of the sulphamic acid and shake the flask until it is dissolved, heating gently should this be necessary. Allow the solution to cool with frequent shaking until about one-fifth of the original amount of solid has separated, as will be the case when the temperature has fallen to between 35 and 40°. This solid is discarded as it contains some of the impurities that may be present. Filter at once through a No. 3 sintered glass crucible into a dry filter flask, which has been placed in a bath of water at about 60°. Transfer the filtrate to a dry conical flask and cool it by rotation under the tap, and finally by surrounding the flask with a mixture of ice and water. Filter through a No. 3 sintered glass crucible and wash the crystals once with a little ice cold water, and three times with small portions of acetone. Dry in an oven at 70° to 80° for ten minutes.

(3) Standardisation of Carbonate-free Normal Sodium Hydroxide by means of Succinic Acid

Weigh accurately 1·5 gram of pure succinic acid on a watch-glass, and wash it into a conical flask with recently boiled and cooled distilled water. Add 2 ml. of phenolphthalein solution, and titrate with the sodium hydroxide to be standardised.

Example of Calculation.—If 25·62 ml. of a sodium hydroxide solution neutralise 1·4930 gram of succinic acid, 1 litre will neutralise $\frac{1 \cdot 4930 \times 1000}{25 \cdot 62}$ grams. But 1 litre of *normal* sodium hydroxide will neutralise 59·04 grams. Therefore the sodium hydroxide solution is

$$\frac{1 \cdot 4930 \times 1000}{25 \cdot 62 \times 59 \cdot 04} = 0 \cdot 987 \text{ N},$$

and contains 40·00 × 0·987 = 39·50 grams NaOH per litre.

Repeat the experiment with another weighed quantity of succinic acid, and calculate the concentration of the sodium hydroxide solution from the result. The experiment should be repeated until results that agree to 2 in 1000 are obtained.

(4) Standardisation of Carbonate-free Decinormal Sodium Hydroxide

Benzoic acid and potassium hydrogen phthalate are more suitable than succinic acid for standardising decinormal sodium hydroxide, on account of their higher equivalent weight.

Benzoic acid should be fused at the lowest possible temperature for about a minute before use. In this compact state it is non-hygroscopic. Weigh out accurately between 0·3 and 0·4 gram, and transfer to a 300 ml. conical flask. Add 20 ml. of alcohol, and cork the flask. When the acid has dissolved, add 1 ml. of phenolphthalein solution, and titrate with the sodium hydroxide solution. (1 litre of decinormal NaOH solution will neutralise 12·212 grams benzoic acid).

Potassium hydrogen phthalate, if not obtainable, is easily prepared by dissolving pure sublimed phthalic anhydride, and slightly more than the calculated weight of pure potassium carbonate to form the acid salt, in water, and mixing the solutions. The acid salt which separates should be purified by recrystallisation from hot water, and dried to a constant weight at 125°. Weigh accurately about 0·5 gram, dissolve in water, and titrate with the sodium hydroxide solution, using phenolphthalein as an indicator. (1 litre of decinormal NaOH solution will neutralise 20·422 grams of potassium hydrogen phthalate.)

STANDARD BARIUM HYDROXIDE (BARYTA) SOLUTION

(*N/20 solution contains* 7·888 *grams* $Ba(OH)_2, 8H_2O$ *per litre*)

The titration of acids, using phenolphthalein or methyl red as indicator, is accurate only if made with an alkali free from carbonate. Commercial sodium hydroxide always contains carbonate, and even when a pure solution is prepared from sodium and water free from carbon dioxide, it soon becomes contaminated with carbonate by exposure to air. Barium and calcium hydroxide solutions, on the other hand, are easily obtained free from carbonate, since the carbonates are nearly insoluble in water (and still less soluble in solutions of the hydroxides), and if protected from carbon dioxide they form

convenient and accurate standard solutions for use with the above indicators.

Preparation of N/20 Baryta Solution.—Dissolve about 35 grams of barium hydroxide [$Ba(OH)_2$, $8H_2O$] and 10 grams of barium chloride in 350 ml. of boiling water contained in a flask, then fit the flask with a cork carrying a soda-lime tube, and set aside until cold. The excess of baryta crystallises, and a clear, saturated solution, which is about 0·35 normal, is obtained.

FIG. 29.

The standard baryta solution must be kept in a bottle which is permanently connected with a burette, atmospheric carbon dioxide being excluded by means of the soda-lime tubes A and B (see Fig. 29). Pour about 2 litres of water into the bottle (a Winchester quart), and connect it with the burette as shown. Remove the soda-lime tube A and insert, temporarily, a piece of ordinary glass tubing in its place. Attach this tube to the water pump, close the burette tap, and draw a current of air free from carbon dioxide through the burette and bottle for ten minutes. (As the soda-lime tube B is small, more efficient purification of a rapid air-current is secured by attaching temporarily a large soda-lime tower to the tube D.) Replace the soda-lime tube A, lift the cork C, carefully decant the cold baryta solution into the bottle, and replace the cork. Mix the contents of the bottle by drawing a current of CO_2-free air through the solution, and fill the burette by opening the clip E and applying suction at D. If the solution is slightly turbid owing to a trace of suspended barium carbonate, allow it to stand overnight before drawing it into the burette. The solution is approximately 0·05 normal, and it may be standardised with pure succinic acid, benzoic acid, potassium hydrogen phthalate, or decinormal hydrochloric acid, using phenolphthalein as indicator.

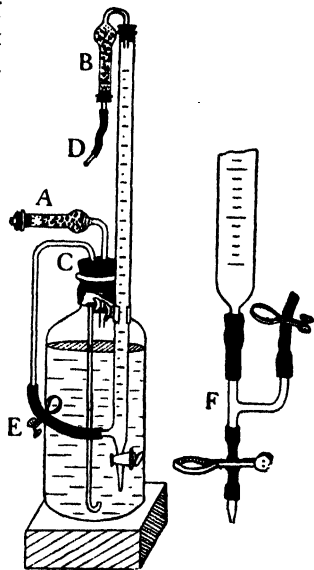
When the burette is not in use, it should be kept filled up above the zero mark, and when used intermittently the first

5 to 10 ml. run out of the burrette are rejected. If a burette with side-tube is not available, an ordinary burette fitted with a T-piece, as shown at F in Fig. 29, is equally convenient. The burette may be fixed in an ordinary clamp, the Winchester resting on the base of the retort stand; or it may be attached to the bottle by means of an Ostwald burette clamp (Fig. 30).

FIG. 30.

STANDARD CALCIUM HYDROXIDE SOLUTION

(*N/25 solution contains* 1·482 *grams* $Ca(OH)_2$ *per litre*)

A saturated solution of calcium hydroxide is about 0·04 normal. It is made by shaking up excess of freshly slaked lime with water in a Winchester quart bottle, which is then set aside for some days until the solution has become clear. The clear solution is then siphoned into another empty Winchester similar to that used for baryta solution, the carbon dioxide in the burette and bottle having been previously removed by means of a current of purified air.

Calcium hydroxide solution is standardised in the same manner as baryta solution.

ANALYSES INVOLVING THE USE OF STANDARD ACID AND ALKALI

Acetic Acid in Vinegar

The acidity of a sample of pure vinegar is due almost entirely to acetic acid, and, even in adulterated vinegar, other acids are rarely found; the total acidity of the vinegar may therefore be attributed to acetic acid. The concentration of acetic acid in commercial vinegars varies widely but is usually between 4 and 5 grams of acetic acid in 100 grams of liquid. The vinegar, whether coloured or not, is titrated with normal sodium hydroxide using phenolphthalein as indicator.

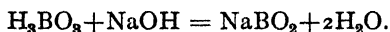
Dilute the measured quantity of vinegar (25 ml.) with about twice as much water, to diminish the loss of acetic acid by volatilisation. Add 2 ml. of phenolphthalein, and titrate the solution at once with normal sodium hydroxide. The first

tinge of pink can be seen even with dark vinegars, but if there is any doubt about the end-point the colour of the solution should be compared with that of the same amount of vinegar diluted to the same extent with water: the colour change is then very readily detected.

Calculate the concentration of acetic acid in grams per litre. It is customary, however, to express the result as the percentage by weight of acetic acid. The density at 15° of 5 per cent. vinegar is about 1·019, and it may therefore be assumed, without serious error, that 1 litre of vinegar weighs 1020 grams. On this basis, calculate the percentage by weight of acetic acid.

Borate in Borax

If boric acid is titrated with sodium hydroxide, using phenolphthalein as indicator, the pink colour appears before all the boric acid is neutralised—on account of hydrolysis of the sodium borate. If glycerol or mannitol is added, the hydrolysis is prevented and the end-point of the titration then corresponds to complete neutralisation of the boric acid, according to the equation

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O.$$

It is therefore possible to determine boric acid by titration with standard sodium hydroxide if glycerol (free from acid) or mannitol is added prior to the titration.

Procedure.—Weigh accurately about 3·5 grams of borax, transfer it to a 300 ml. beaker, and dissolve it in about 180 ml. of water. Add 2 ml. of methyl orange, and then dilute hydrochloric acid until the solution is slightly acid. Then run in dilute (about decinormal) sodium hydroxide until the solution is neutral to methyl orange. (The solution now contains sodium chloride and boric acid.) Transfer the solution to a 250 ml. standard flask, dilute to the graduation mark with water, and mix thoroughly.

Determine whether the glycerol that is to be used is neutral. If a 5 ml. sample, to which phenolphthalein has been added, does not give a pink coloration with the first drop of a very dilute (about centinormal) sodium hydroxide solution, take a larger sample, add phenolphthalein, and then sodium hydroxide until a faint pink coloration is obtained.

To 25 ml. of the prepared boric acid solution, add 15 ml. of glycerol, and titrate with decinormal sodium hydroxide, using phenolphthalein as indicator. The end-point is reached when the yellowish solution shows a pink coloration. The pink colour should persist on the addition of a little more glycerol; should it disappear, continue the titration until the pink colour is no longer discharged by the addition of more glycerol. The sodium hydroxide must be free from carbonate. If mannitol is used instead of glycerol, 2 to 3 grams is sufficient.

Calculate the percentage of B_2O_3 in the sample of borax and also the corresponding percentage of anhydrous borax, $Na_2B_4O_7$.

Sulphuric Acid in the Concentrated Acid

The concentration of sulphuric acid in the commercial product is usually expressed as the percentage by weight of H_2SO_4, *i.e.* the number of grams of H_2SO_4 in 100 grams of solution, and it may be very roughly ascertained by finding the density of the acid and consulting the table given on p. 481. Since the density of sulphuric acid attains a maximum at about 97 per cent., and varies but little with the concentration above 94 per cent., a more accurate determination of the percentage of H_2SO_4 in a sample of the commercial acid may be made by titration, as follows :—

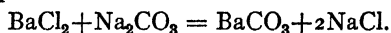
Weigh accurately in a tared weighing-bottle about 13 grams (about 7 ml.) of the concentrated acid. (Since the acid is hygroscopic, avoid unduly exposing it to the air.) Two-thirds fill a 250 ml. standard measuring-flask with water, and pour in through a funnel as much as possible of the acid. Wash in the remainder by means of a jet of water. Rinse the funnel and remove it. Mix the acid and water thoroughly by imparting a rotary movement to the liquid, and cool under the tap until the liquid is at the room temperature. Dilute to the graduation mark, and mix thoroughly.

Titrate portions of 25 ml. with normal sodium hydroxide, using methyl red or methyl orange as indicator. From the results, calculate the percentage by weight of H_2SO_4 in the original concentrated acid.

Alkaline Earth Metals in Solution as Chloride or Nitrate

Exercise.—Barium Chloride in the Bench Reagent.

METHOD 1.—By titrating a neutral solution of barium chloride with normal sodium carbonate, the solution remains neutral until all the barium is precipitated as carbonate. The least excess of sodium carbonate is indicated in this special case by phenolphthalein :

$$BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl.$$

Assuming that the bench barium chloride is approximately N/2, titrate a measured volume directly with normal sodium carbonate, using phenolphthalein as indicator.

METHOD 2.—To the neutral barium chloride solution is added an amount of standard sodium carbonate solution more than sufficient to precipitate all the barium as carbonate. The excess of sodium carbonate remaining is found by titration with standard acid, and the amount used in precipitating the barium obtained by difference.

Measure out 25 ml. of bench barium chloride solution, dilute to about 100 ml., and slowly run in from a burette 50 ml. of normal sodium carbonate. Heat to boiling, and maintain the temperature until the barium carbonate has become crystalline and settles rapidly. Cool, make up to 250 ml. in a standard flask, and mix thoroughly. Filter through a dry paper, neglecting the first few millilitres, and titrate 50 ml. of the filtrate with seminormal hydrochloric acid, using methyl orange as indicator. A correction may be applied for the volume of the barium carbonate precipitated, assuming that the density of this is about 4.

Mixture of Alkali Hydroxide and Carbonate

METHOD 1.—The total alkali is determined in one part of the mixture, whilst in another part the carbonate is precipitated by adding excess of barium chloride (which must be neutral), leaving the hydroxide still in solution. This is then titrated without filtering off the barium carbonate.

Exercise.—Prepare a mixture of sodium hydroxide and sodium carbonate of known strength by measuring 100 ml. of N/10 NaOH (carbonate free) and 100 ml. of N/10 Na_2CO_3

into a 250 ml. flask, making up to the mark, and mixing thoroughly.

Titrate 25 ml. of this mixture with N/10 HCl, using methyl orange. This gives the acid equivalent to the total alkali in 25 ml.

Place 50 ml. of the mixture in a conical flask, add 100 ml. of water, and without heating add slowly just a slight excess of barium chloride solution over that required to precipitate the carbonate. This can be done if the concentration of the barium chloride solution is known (see previous Exercise) by calculating the exact volume of barium chloride solution which should be used and adding 1 ml. in excess. Mix thoroughly and allow to stand for a few minutes. Add 1 ml. of phenolphthalein and titrate the hydroxide remaining in solution with N/10 HCl. The acid must be added *very slowly* with constant shaking, especially near the end-point, in order to avoid interaction with the barium carbonate before the phenolphthalein is decolorised. To decrease the risk of this, N/100 acid may be used to finish the titration.

The second titration gives the volume of N/10 HCl equivalent to the original sodium hydroxide in 50 ml., and the difference between the first titration and half the second gives the volume of N/10 HCl equivalent to the carbonate in 25 ml. of the mixture.

If the carbonate content of the mixture is unknown, it is difficult to ascertain when a slight excess of barium chloride has been added. Since the use of a large excess of this reagent leads to low results for the sodium hydroxide, a rough trial must first be made, adding barium chloride equivalent to the total alkali. The second part of the analysis is then repeated, adding, on this occasion, just a slight excess as indicated by the approximate result for the carbonate determination.

METHOD 2.—By titrating with dilute hydrochloric acid in the presence of a suitable indicator, the point at which the hydroxide present has been neutralised and the carbonate converted to bicarbonate can be determined. Both phenolphthalein and cresol red have been used, but these indicators show the colour change too late. On the other hand, a mixture of cresol red and thymol blue shows a colour change very close to the required point. This mixed indicator is prepared by dissolving 0·16 gram of thymol blue and 0·027 gram of cresol

red in water containing 4·6 ml. of decinormal sodium hydroxide, and diluting the solution to a litre, 1 ml. being required for each titration. In alkaline solution the colour is blue, and this changes to pale yellow when sufficient acid has been run into the hydroxide and carbonate mixture. The acid must be added slowly specially near the end-point. The titration is then continued after the addition of methyl orange or, better, bromo-phenol blue, until the change in colour of this indicator shows the complete decomposition of the bicarbonate.

The acid used for the second part of the titration is equivalent to half the total carbonate present, and the difference between the first and second titrations gives the acid equivalent to the hydroxide.

If V_1 = the volume of N/10 HCl required to change the colour of the mixed indicator,

and V_2 = the additional volume of N/10 HCl required to change the colour of methyl orange,

then the weight of Na_2CO_3 in the volume of mixture taken

$$= 2V_2 \times 0{\cdot}0053 \text{ grams,}$$

and the weight of NaOH = $(V_1 - V_2) \times 0{\cdot}004$ grams.

Mixture of Alkali Carbonate and Bicarbonate

Both the methods described above for the analysis of a mixture of alkali hydroxide and carbonate may be used for a mixture of carbonate and bicarbonate, though the first method requires some slight modification.

METHOD 1.—The total alkali is determined by titration with N/10 HCl using methyl orange. Before the addition o' barium chloride solution to another portion of the mixt· add a known volume of N/10 NaOH, which must be in of that required to convert the bicarbonate to normal car· assuming that all the alkali is present as bicarbor procedure of Method 1 is now followed.

The calculation is made as follows. The dif the volume of N/10 NaOH added to the found by titration after the addition of equivalent to the bicarbonate origina' and the value obtained for the total of carbonate can be found.

If V_1 = the volume of N/10 NaOH added to the mixture taken,

V_2 = the volume of N/10 HCl required, after precipitation of the carbonate by $BaCl_2$, to change the colour of phenolphthalein,

V_3 = the volume of N/10 HCl required in the titration of another equal portion of the mixture, using methyl orange as indicator,

then the weight of $NaHCO_3$ in the volume taken

$$= (V_1 - V_2)\ 0{\cdot}0084 \text{ grams,}$$

and the weight of $Na_2CO_3 = [V_3-(V_1-V_2)]\ 0{\cdot}0053$ grams.

METHOD 2.—In this case the acid required to change the colour of the mixed indicator (p. 88) is equivalent to half the carbonate, whilst the additional volume of acid required to change the colour of methyl orange is equivalent to the bicarbonate and half the carbonate.

If V_1 = the volume of N/10 HCl required to change the colour of the mixed indicator,

and V_2 = the additional volume of N/10 HCl required to change the colour of methyl orange,

then the weight of sodium carbonate in the volume taken

$$= 2V_1 \times 0{\cdot}0053 \text{ grams,}$$

and the weight of sodium bicarbonate

$$= (V_2 - V_1) \times 0{\cdot}0084 \text{ grams.}$$

Hydroxide and Carbonate in Lime

(1) Determine the total alkali (hydroxide plus carbonate) follows :—Weigh accurately about 0·8 gram of the powdered
nd transfer to a conical flask. Add 25 ml. of normal
loric acid, and warm gently until the lime has dissolved.
uantity of insoluble matter usually remains.) Cool
nd titrate the excess of acid with normal sodium
methyl orange as indicator. (The colour of
fades gradually during this titration, and
at intervals.)

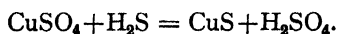
droxide as follows :—Weigh accurately
dered lime, and transfer it to a dry,
Add from pipettes 2 ml. of alcohol

and 100 ml. of a 10 per cent. sugar solution, to form a soluble calcium sucrate. (The alcohol prevents the lime forming lumps when the sugar solution is added.) Shake the bottle more or less continuously for about half an hour. Filter through a dry paper and collect the filtrate (after rejecting the first 5 ml.) in a dry beaker. Titrate 50 ml. of the filtrate with normal hydrochloric acid, using methyl orange as indicator.

From the results obtained in (1) and (2), calculate the percentages of calcium hydroxide and calcium carbonate in the lime. In calculating the former, it may be assumed that the volume of the whole filtrate in (2) is 102 ml.

Acidic Radical in Salts of Heavy Metals

A solution of the salt is decomposed by means of hydrogen sulphide whereby an insoluble sulphide is precipitated and an equivalent amount of acid remains in solution ; *e.g.*,

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

After separating the insoluble sulphide by filtration, the acid filtrate is titrated with standard alkali. This method is applicable to the determination of the acidic radical in many salts of the heavy metals. It is assumed that no free acid is present in the original solution except that derived from hydrolysis of the salt.

Exercise.—Dissolve about 0·25 gram (accurately weighed) of copper sulphate in hot water, add about 2 grams of pure sodium chloride, and precipitate the copper with hydrogen sulphide. Filter and wash the precipitate with hydrogen sulphide solution (*cf.* pp. 36 and 365). Boil the mixed filtrate and washings until most of the hydrogen sulphide is expelled. Cool, and titrate with *decinormal* sodium hydroxide, using methyl orange as indicator.

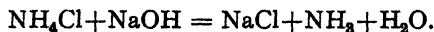
Calculate the percentage of SO_4 in the salt.

Chloride may be determined in the same way in the case of a copper or mercuric salt.

Ammonia (*Indirect Method*)

(1) When an ammonium salt, such as ammonium chloride, is decomposed by boiling with an excess of sodium hydroxide

solution, ammonia is liberated and an equivalent amount of sodium hydroxide is used up, in accordance with the equation:

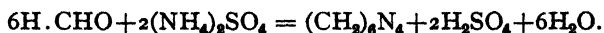
$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O.$$

If a known quantity of sodium hydroxide (in excess of that required to decompose the ammonium salt) is used, and if, after the decomposition is complete, the residual sodium hydroxide is determined, the difference between these quantities gives the amount of sodium hydroxide equivalent to the ammonium salt taken.

If the ammonium salt contains free acid, the solution must be accurately neutralised before adding a measured excess of alkali; or the amount of acid present must be determined by a separate titration and allowed for in the calculation. The ammonium radical in salts like ferrous ammonium sulphate cannot be determined by this method, as part of the sodium hydroxide is used up in the precipitation of the hydroxide of the heavy metal.

Procedure.—Weigh accurately about 1 gram of the substance (*e.g.* ammonium sulphate), wash it into a 250 ml. conical flask, and dilute the solution to about 75 ml. Add a measured excess (that is an amount which is more than sufficient to decompose the ammonium salt) of normal sodium hydroxide solution (25 ml.) and boil gently to expel the ammonia. At intervals of about five minutes, test for ammonia in the escaping steam with a piece of moist red litmus paper—the test paper being held outside the flask. When the decomposition is complete, *i.e.* when no ammonia can be detected in the steam, cool the solution and titrate with standard hydrochloric acid, using methyl red as indicator.

Calculate the percentage of NH_3 in the substance.

(2) Another method makes use of the reaction between formaldehyde and ammonium salts, whereby hexamethylenetetramine is formed, and the acid originally combined with the ammonia is liberated:

$$6H.CHO + 2(NH_4)_2SO_4 = (CH_2)_6N_4 + 2H_2SO_4 + 6H_2O.$$

Procedure.—Dissolve a weighed quantity of the ammonium salt (*e.g.* 0·4 to 0·5 gram of ammonium sulphate) in water and dilute the solution to 100 ml. in a standard flask. Place 25 ml. of the solution in a conical flask, add 5 ml. of formalin (previously rendered very faintly alkaline to phenolphthalein by addition

of sodium hydroxide) and after a few minutes, titrate the solution with decinormal sodium hydroxide, using phenolphthalein as indicator.

Ammonia (*Direct Method*)

OUTLINE OF METHOD.—The substance is boiled with excess of sodium hydroxide solution, and the ammonia evolved is absorbed either (*a*) by a known volume of a standard acid solution, and the amount of acid neutralised by the ammonia determined by titration of the excess of acid with standard alkali; or (*b*) by a saturated solution of boric acid, and titrated directly by standard acid, using an indicator which is unaffected by free boric acid.

METHOD (*a*).—Arrange the apparatus as shown in Fig. 31. A is a copper flask of about a litre capacity. (A round-bottomed resistance-glass flask of about 500 ml. capacity may be used instead of the copper flask.[1]) Fit the flask with a two-holed rubber cork to carry the tap-funnel C and the tube leading to the condenser. It is advisable to have a trap at D to prevent any drops of sodium hydroxide being driven over during the boiling.[2] Wet the inner tube of the condenser with water, and attach a boiling-tube with a hole in the bottom. B is a 500-600 ml. beaker. A convenient arrangement is to place B on a wood block, so that the beaker can be lowered or removed by taking away the block.

Examine the apparatus carefully to be sure that there is no leakage at any of the corks. Introduce into the tap-funnel a known quantity [3] of the substance to be analysed, and wash it into the flask with water. In the beaker B place a measured volume (25 or 50 ml.) of normal hydrochloric acid, and add to it an equal volume of water and 2 ml. of methyl red.

When these preparations are completed, run into the large flask through the tap-funnel an excess of sodium hydroxide

[1] A better arrangement is to pass a current of steam from a separate generating vessel through the gently heated liquid. This entirely prevents any bumping in the alkaline solution. The alkali for decomposition is added previously down the tube by which the steam enters.

[2] The trap is more efficient if a hole is made in the *side* of the tube leading from the copper flask into D; the hole must be situated below the rubber stopper.

[3] In general, the amount of an unknown substance to be taken for analysis must be regulated by the result of a rough quantitative test.

solution, and close the tap as soon as all the alkali has entered. As a rule about 50 ml. of 2N sodium hydroxide will be sufficient. Add sufficient distilled water (200 ml.) to ensure that the contents of A will not be evaporated to dryness during the experiment.

It is of course essential that all the ammonia evolved should be caught by the standard acid in the absorption flask. The only risk of loss is while the air in the large flask is being expelled. Apply heat therefore, cautiously, so that there is no sudden rush of gas through the standard acid. Boil for thirty minutes. In that time all the ammonia should be over, but it is well to make sure. Disconnect at E, and test the distillate with litmus paper. If it is still alkaline, the boiling must be continued.

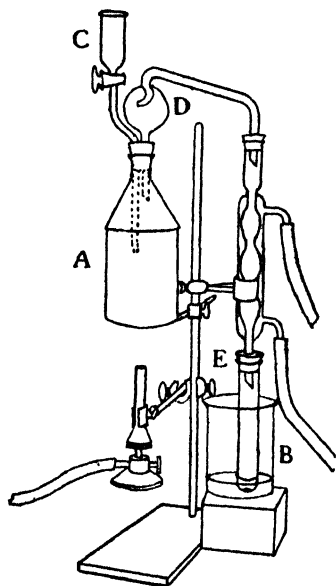



FIG. 31.

When all the ammonia has been driven over, *open the tap C before extinguishing the flame*, disconnect the apparatus and titrate the solution in B to find how much of the acid remains unneutralised.

In order to avoid overstepping the end-point when titrating the large volume of liquid, proceed as follows :—Transfer about one-third of the liquid in B to a smaller beaker. Run standard alkali into the main portion in B until the neutral point is slightly overstepped. Add about one-half of the portion in the small beaker, then more standard alkali as before, followed by more of the reserve portion, and so on until all the reserve portion has been added, when the end-point can be accurately adjusted. Finally, pour some of the neutral liquid into the small beaker, pour it back into B, and add a further half-drop of alkali if required.

Another Absorption Apparatus.—The apparatus described above for the absorption of the ammonia has the advantage of simplicity, and there is little risk of losing ammonia if the heating

is carefully regulated. With the form of absorption apparatus shown in Fig. 32, there is much less risk of losing ammonia. The flask is fitted with a two-holed rubber cork carrying an adapter G for the end of the condenser and a tube H filled with glass beads. At the start of an experiment with this form of apparatus, the measured volume of standard acid is run in through the tube H so as to moisten the beads with acid. One or two drops of methyl red are then poured on the beads; the red coloration produced must persist to the end of the distillation.

When all the ammonia has been driven over, the liquid in H is washed down into the flask prior to the titration.

FIG. 32.

Exercise.—Determine the percentage of NH_3 in ammonium sulphate. Use from 1·3 to 1·5 gram (accurately weighed).

METHOD (*b*).—The same apparatus is used as in Method (*a*), but the ammonia evolved is absorbed by about 100 ml. of saturated boric acid, instead of by a fixed quantity of standard acid. This method possesses advantages in that the use of standard alkali is eliminated, and there is no need to measure accurately the volume of boric acid solution used. The weight of ammonium salt taken should not be more than will yield about 0·07 gram of ammonia. The boric acid solution may be made by dissolving 10 grams of pure boric acid in 250 ml. of warm water, and cooling. After the distillation has proceeded for thirty minutes, or until about 100 ml. has passed over, the absorbed ammonia is titrated with decinormal hydrochloric acid, using methyl orange (or better, bromo-phenol blue) as indicator.

Nitrate

The nitrate is reduced to ammonia by means of (*a*) Devarda's alloy (Al, 45; Cu, 50; Zn, 5) and sodium hydroxide, or (*b*) titanous sulphate or chloride and sodium hydroxide. The ammonia is then determined in the usual manner.

Procedure.—(*a*) Place a weighed portion of the substance (0·3 to 0·5 gram) in a 500 ml. resistance-glass flask, add 100 ml. of water, and 3 grams of Devarda's alloy. This should be in the form of a coarse powder free from fine dust. Use the same apparatus as described under the estimation of ammonia (p. 93).

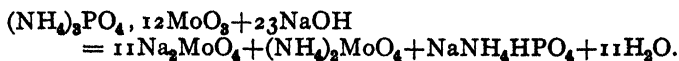
When the apparatus is fitted up and the absorbing liquid ready in the beaker, place about 25 ml. of nearly saturated sodium hydroxide solution (18 grams NaOH dissolved in 20 ml. water) in the tap-funnel, and run about one-third of this into the flask. Warm gently, and add the remaining sodium hydroxide gradually, keeping the reaction under control by cooling the flask with water if necessary. Finally, the contents of the flask are gently heated without boiling for about an hour, because of the danger of carrying over sodium hydroxide spray, after which time the distillation of the ammonia may be carried out by boiling. This is continued for about half an hour, and the ammonia collected is determined as described in the previous experiment.

(*b*) Place a weighed portion (about 0·15 gram) in the copper or glass flask, and add about 100 ml. of 2 N sodium hydroxide solution. While swirling the contents of the flask, add 25 ml. of commercial titanous sulphate or chloride (15 per cent. solution). Without delay, connect the flask with the condenser, add about 150 ml. of water through the tap-funnel, and distil off the ammonia into the absorbing liquid.

Exercise.—Determine the percentage of sodium nitrate in a sample of the commercial salt (Chili nitre). For (*a*) use about 0·4 gram and collect the ammonia in 25 ml. of normal acid, or in 150 ml. of saturated boric acid. For Method (*b*) dissolve about 1·5 gram in water and dilute the solution to 250 ml. in a standard flask. Use 25 ml. of this solution and collect the ammonia in 25 ml. of decinormal acid, or in 100 ml. of saturated boric acid.

Phosphate

The phosphate is precipitated as ammonium phosphomolybdate and the precipitate is filtered and washed. It is then treated with a measured volume of standard sodium hydroxide, and the excess of the latter is titrated with standard acid :

$$(NH_4)_3PO_4, 12MoO_3+23NaOH$$
$$= 11Na_2MoO_4+(NH_4)_2MoO_4+NaNH_4HPO_4+11H_2O.$$

From the above equation it may be seen that 1 gram-atom of phosphorus requires 23 gram-molecules of sodium hydroxide,

and therefore 1 litre of decinormal alkali is equivalent to 0·1349 gram of phosphorus, or 0·3088 gram of phosphorus pentoxide.

Procedure.—Place a measured volume of the phosphate solution, containing not more than 10 milligrams of P_2O_5, in a 400 ml. flask, add 10 grams of ammonium nitrate and 5 ml. of concentrated nitric acid. Add water to give a volume of about 100 ml. Measure 50 ml. of a freshly prepared 3 per cent. ammonium molybdate solution into another flask. Heat these solutions to between 40° and 45°, and add the ammonium molybdate solution slowly to the phosphate mixture, using a dropping-tube (p. 236), and shaking continuously. It is important not to heat the solutions over 45°, in order to avoid contaminating the precipitate with molybdic acid.

The flask is now fitted with a rubber stopper, shaken vigorously for five minutes, and left to stand for half an hour. Filter through paper pulp on a 1 cm. perforated porcelain disc (p. 37). Transfer the precipitate to the filter, and wash the flask and the precipitate with 1 per cent. potassium nitrate solution until the filtrate is not acid to methyl orange. This will require about 100 ml. of washing liquid. Now return the precipitate together with the paper pulp and porcelain disc to the flask in which the precipitation was carried out. Add from a pipette 50 ml. of decinormal sodium hydroxide free from carbonate, which will be more than enough to dissolve the yellow precipitate completely. The alkali must be added through the funnel in which the filtration took place, in order to dissolve the precipitate which remains on the sides, and the funnel must be rinsed into the flask with distilled water.

Shake the flask until all the yellow precipitate is dissolved, add phenolphthalein, and titrate with decinormal hydrochloric acid until the pink colour is completely discharged.

Exercise.—Determine the percentage of P_2O_5 in microcosmic salt, $NaNH_4HPO_4, 4H_2O$. (This is a more reliable standard than potassium dihydrogen phosphate, which is often used. If it is to be recrystallised, a little ammonia should be added to replace that lost when the solution is hot. See *Ind. Eng. Chem.*, 1924, p. 1268.) Weigh accurately between 0·2 and 0·25 gram of microcosmic salt, dissolve it in water, and dilute to 250 ml. in a standard flask. Mix thoroughly, and use 25 ml. for each determination.

Determination of Phosphorus in Iron.—Place a weighed

quantity of the metal (about 2 grams of steel or 0·4 gram of cast iron) in a covered 300 ml. beaker, add 30 ml. of water and 10 ml. of concentrated nitric acid, and warm on a hot-plate until the metal has dissolved. Add 30 ml. of decinormal potassium permanganate solution and boil for three minutes to destroy carbides and complete the oxidation of the phosphorus. The boiling must be continued until the pink colour disappears. Then add enough ferrous sulphate (containing sulphuric acid) to dissolve the precipitated manganese dioxide. Boil the solution to expel oxides of nitrogen. Rinse the cover-glass and add 10 grams of ammonium nitrate and 5 ml. of concentrated nitric acid and filter if necessary. Precipitate the phosphate at 40° to 45° by adding 50 ml. of ammonium molybdate solution, and complete the determination by the alkalimetric method described above.

In this case, however, the precipitate must first be washed with 0·1N nitric acid until free from iron, and then with 1 per cent. potassium nitrate solution until free from acid.

From the data obtained, calculate the percentage of phosphorus in the sample.

In the case of a high-chromium or stainless steel, dissolve 2 grams of the sample in 20 ml. of 60 per cent. perchloric acid in a 500 ml. conical flask, warming to effect solution. Boil for thirty minutes, with a small funnel in the mouth of the flask, to ensure complete oxidation. Cool the deep red solution, dilute to 100 ml., and add ammonium hydroxide of 0·9 sp. gr. (p. 483) until a slight precipitate is formed. Dissolve this by the addition of about 20 ml. of nitric acid of 1·2 sp. gr. (p. 482). Add a few ml. of 10 per cent. ammonium bisulphite to reduce the chromate present. Boil to remove nitrous fumes and free chlorine, add 10 grams of ammonium nitrate and 5 ml. of concentrated nitric acid, filtering if necessary, and precipitate the phosphate as described above.

Persulphate

Some persulphates can be determined by boiling their aqueous solutions and titrating the sulphuric acid set free :

$$2K_2S_2O_8 + 2H_2O = 2K_2SO_4 + 2H_2SO_4 + O_2.$$

The decomposition, which is slow even at the boiling-point, can be accelerated by the addition of a solution of silver nitrate.

Weigh accurately between 0·3 and 0·4 gram of the sample of potassium persulphate, and dissolve it in 100 ml. of water. Add methyl red and if the solution is acid owing to the presence of some bisulphate, run in decinormal sodium hydroxide until it is neutral. Then add about 10 ml. of decinormal silver nitrate, and boil for not less than ten minutes. Cool, again add methyl red, and titrate with decinormal sodium hydroxide.

Ammonium persulphate does not give accurate results by this method, because some nitric acid is formed owing to partial oxidation of the ammonium radical. For a better method, see p. 115.

Reduction - Oxidation Processes

OXIDATION and reduction necessarily occur together, one substance being oxidised as another is reduced. The theory of these reactions is dealt with under Electrometric Methods on p. 197. Reactions described as oxidations are usually those in which the oxidising agent forms the standard solution, whilst in those classified as reductions a standard solution of the reducing agent is employed.

A considerable number of reagents are used in the form of standard solutions. The following table contains those usually employed :—

Oxidising Agents.	Reducing Agents.
Potassium permanganate.	Sodium thiosulphate.
Potassium dichromate.	Arsenious acid.
Ceric sulphate.	Titanous sulphate.
Iodine.	
Potassium bromate.	
Potassium iodate.	

When using reagents such as potassium permanganate, which are deeply coloured themselves but give colourless solutions after reacting, no indicator is required. In other cases some additional substance must be added which will serve as an indicator. The theory underlying the use and action of a reduction-oxidation indicator will be dealt with later (p. 200).

STANDARD POTASSIUM PERMANGANATE

(*N*/10 *solution contains* 3·161 *grams* $KMnO_4$ *per litre*)

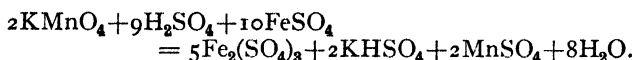
Nearly all of the determinations commonly made with potassium permanganate are carried out in an acid solution. Hydrochloric acid is avoided, if possible, because it may be oxidised by the permanganate (see p. 121), and since nitric acid, like the permanganate, is an oxidising agent, its presence is not desirable. Sulphuric acid is the most suitable acid,

and it is almost always added in titrations that are to be carried out with permanganate in an acid solution.

Potassium permanganate in presence of sulphuric acid oxidises ferrous sulphate as follows :—

$$2KMnO_4+4H_2SO_4 = 2KHSO_4+2MnSO_4+3H_2O+5[O]$$
$$10FeSO_4+5[O]+5H_2SO_4 = 5Fe_2(SO_4)_3+5H_2O$$

or, combining these equations,

$$2KMnO_4+9H_2SO_4+10FeSO_4 = 5Fe_2(SO_4)_3+2KHSO_4+2MnSO_4+8H_2O.$$

The first equation shows that two molecules of the permanganate provide five atoms of available oxygen. A solution that contains one-fifth of the molar weight per litre will provide 8 grams of oxygen per litre and is described, therefore, as a normal solution. A decinormal solution contains one-fiftieth of the molar weight per litre, *i.e.* 3·161 grams.

Standard solutions of potassium permanganate should be prepared from a well-crystallised specimen of the salt, in the form of brilliant black crystals with a metallic lustre, free from any blue or violet iridescence. A solution prepared from the pure salt and water free from organic matter is very stable, but the salt of commerce (including some brands described as " for analysis ") usually contains a small quantity of manganese dioxide, and this impurity brings about progressive decomposition of the solution, slowly at first and afterwards more rapidly. If the suspended oxide is completely removed by careful filtration, the solution will remain unchanged for many months if kept in the dark.

Weigh about 3·2 grams of potassium permanganate. Transfer the crystals (which must not be powdered) to a clean flask and add about 500 ml. of cold distilled water. Shake the flask at intervals and set it aside overnight. Filter the solution through a funnel containing a plug of glass-wool covered with a little asbestos into a filter-flask, and dilute to the mark in a graduated litre flask with freshly boiled and cooled distilled water. Transfer the solution to a thoroughly clean, glass stoppered bottle. (The flasks and bottle must first be cleaned with chromic acid solution and afterwards rinsed with distilled water.)

More certain removal of manganese dioxide will be accomplished by filtering through a No. 4 sintered glass crucible

(p. 214). This can be carried out automatically by fitting a rubber bung just into the top of the crucible. A glass tube bent twice at right angles passes through the bung so that the end is almost touching the glass filter, thus preventing any possibility of the solution coming into contact with the rubber. The other end of the tube dips into the flask containing the permanganate. By the use of a screw-clip on the tubing between the filter flask and the pump the water may be turned off after a partial vacuum has been established.

On account of the action of potassium permanganate solution on rubber, the burette used for the solution must have a glass tap. Since the meniscus cannot be clearly seen through the deep purple solution (unless it is very dilute), the burette readings are taken at the highest level of the liquid surface which, against a white card, appears as a sharp, horizontal line. A burette that has been used for permanganate solution should be emptied and cleaned immediately after use. Brown stains of manganese oxides can be removed with sulphurous acid, or with acidified ferrous sulphate.

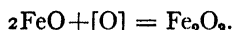
As already explained, most permanganate titrations are carried out in presence of sulphuric acid, and sufficient acid must be added—*before beginning the titration*—to prevent the formation of a permanent brown coloration or a brown precipitate. The permanganate solution must be run in slowly, with continuous stirring or very frequent shaking. No indicator other than the permanganate itself is required, and the end-point of the titration is easily recognised. A single drop of decinormal permanganate solution is sufficient to impart a distinct pink colour to 200 ml. of water. An endeavour should be made to keep the volume of the solution at the end-point of all titrations as nearly constant as possible —in general, about 100 ml.—in order that a constant excess of permanganate will be required to give the same intensity of pink colour. Greater accuracy will thereby result.

Permanganate solutions may be standardised with ferrous ammonium sulphate, arsenious oxide, sodium oxalate, oxalic acid, or potassium tetroxalate, all of which are obtainable as "analytical reagents" of a definite standard of purity. Arsenious oxide and sodium oxalate are the best standards for the purpose.

Standardisation with Ferrous Ammonium Sulphate.—

The formula of ferrous ammonium sulphate is $FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$. Weigh accurately from 1·0 to 1·1 gram, wash into a conical flask with 4N sulphuric acid,[1] dilute the solution to about 70 ml., and run in the permanganate solution slowly, with frequent shaking, until a faint permanent pink coloration is obtained.

Calculation.—The oxidation of a ferrous to a ferric compound may be represented in its simplest form by the equation

$$2FeO + [O] = Fe_2O_3.$$

It is evident that 55·84 grams of iron are oxidised by 8 grams (1 gram-equivalent) of oxygen. But the molar weight (392·1 grams) of ferrous ammonium sulphate contains 55·84 grams of iron, and is oxidised therefore by 8 grams of oxygen, *i.e.* by 1 litre of normal permanganate.

If 26·80 ml. of the permanganate oxidises 1·052 gram of ferrous ammonium sulphate,

$$1 \text{ litre will oxidise } \frac{1{\cdot}052 \times 1000}{26{\cdot}80} \text{ grams.}$$

But 1 litre of normal permanganate will oxidise 392·1 grams. Therefore the permanganate solution is

$$\frac{1{\cdot}052 \times 1000}{26{\cdot}80 \times 392{\cdot}1} = 0{\cdot}1001\text{N}.$$

Standardisation with Arsenious Oxide.—For accurate results with this standard the presence of a suitable catalyst is necessary, a trace of potassium iodide or iodate being usually employed.

Weigh out accurately into a 400 ml. beaker about 0·25 gram of pure dry arsenious oxide, As_2O_3 (see p. 159), and add about 10 ml. of a 20 per cent. solution of pure sodium hydroxide. Stir until the solid has dissolved, add 100 ml. of water, 10 ml. of concentrated hydrochloric acid, and *one* drop of a 0·05 per cent. potassium iodide solution. Titrate with potassium permanganate, which must be added drop by drop near the end, allowing the colour to disappear completely before the next drop is added. The reaction is finished when the pink colour persists for thirty seconds.

[1] It is advisable that ferrous salt solutions should be not less than 2N with respect to sulphuric acid in order to minimise atmospheric oxidation.

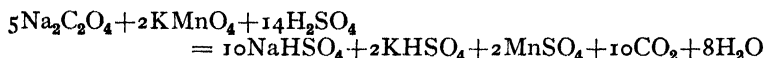
From the reading obtained, deduct the volume of potassium permanganate required to give the same depth of colour to the same final volume of liquid containing the same amounts of sodium hydroxide, acid, and catalyst.

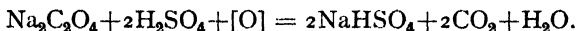
The gram equivalent of arsenious oxide is 49·46.

Standardisation with Sodium Oxalate.—Sodium oxalate, $Na_2C_2O_4$, is an anhydrous salt, and it may be dried before use by heating in an air-oven for an hour at 120°.

Weigh accurately from 0·17 to 0·19 gram of the salt. Wash it into a conical flask, add 30 ml. of dilute sulphuric acid, and dilute to about 70 ml. Heat the solution to about 90° (just short of boiling). Titrate the hot solution by running in the permanganate *very slowly*, while shaking the flask continuously. See that the temperature does not fall below 60°, and allow each drop (or half-drop) of permanganate to become completely decolorised before adding the next. A very faint, permanent pink coloration marks the end-point. (The formation of a brown precipitate or a permanent brown coloration during the titration indicates that the solution is too cold, or that the permanganate has been added too quickly, or that insufficient sulphuric acid is present.) Repeat the titration with another weighed portion of the sodium oxalate.

The oxidation of sodium oxalate by potassium permanganate in presence of sulphuric acid may be represented by the equation

$$5Na_2C_2O_4+2KMnO_4+14H_2SO_4$$
$$= 10NaHSO_4+2KHSO_4+2MnSO_4+10CO_2+8H_2O$$

or in simpler form by the equation

$$Na_2C_2O_4+2H_2SO_4+[O] = 2NaHSO_4+2CO_2+H_2O.$$

It may be seen from the second equation that 1 molar weight of sodium oxalate (134·0 grams) requires 16 grams of oxygen. Therefore 67·0 grams of sodium oxalate require 8 grams of oxygen, or 1 litre of normal permanganate solution.

Alternative Method of Standardisation with Sodium Oxalate.—The above method for standardising potassium permanganate by sodium oxalate in hot acid solution has recently been shown (*J. Res. Nat. Bur. Stan.*, 1935, xv. 493) to give a value for the normality which is about 0·4 per cent. higher than that obtained using arsenious oxide or standard ferrous solutions. The following procedure gives results which

agree closely with those obtained when these other standards are used.

Weigh accurately about 0·3 gram of sodium oxalate, which has been dried at 105°, into a 600 ml. beaker. Add 250 ml. of a solution of sulphuric acid prepared by adding 15 ml. of concentrated sulphuric acid to 285 ml. of water, boiling for ten minutes and cooling to $27° \pm 3°$. After the oxalate has dissolved, add 40 ml. of the approximately N/10 potassium permanganate, running in about 30 ml. per minute with gentle stirring, keeping the temperature at about 27°. When the pink colour has disappeared, heat to between 55° and 60°, and run in the potassium permanganate until a very faint pink colour persists for half a minute, adding the last millilitre slowly, allowing the colour due to each drop to disappear before the next is added. It is advisable to carry out a " blank " experiment, omitting the sodium oxalate, and working to approximately the same depth of colour at the end-point.

Oxalic acid, $H_2C_2O_4, 2H_2O$, or **Potassium tetroxalate,** $KHC_2O_4, H_2C_2O_4, 2H_2O$, may be used instead of sodium oxalate for the standardisation, but being hydrates they are less reliable. One litre of decinormal permanganate solution will oxidise 6·303 grams of oxalic acid and 6·355 grams of the tetroxalate, and from 0·16 to 0·18 gram of either substance is required for a single titration.

ANALYSES INVOLVING THE USE OF STANDARD PERMANGANATE

Iron

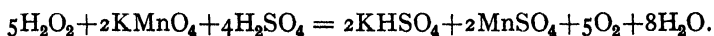
One of the most important determinations that can be made by means of a standard solution of potassium permanganate is that of iron (p. 103). Iron can be determined, however, equally well with standard potassium dichromate, and all the examples of analysis involving the determination of iron are given after the preparation and use of a standard dichromate solution have been described (see p. 117).

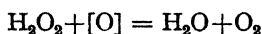
Oxalic Acid and Oxalates

The procedure is described under the standardisation of permanganate with sodium oxalate.

Peroxides

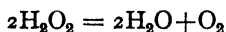
Hydrogen Peroxide.—In presence of sulphuric acid, hydrogen peroxide and potassium permanganate solutions interact as follows :—

$$5H_2O_2+2KMnO_4+4H_2SO_4 = 2KHSO_4+2MnSO_4+5O_2+8H_2O.$$

The decomposition of the hydrogen peroxide may be represented more simply by the equation

$$H_2O_2+[O] = H_2O+O_2$$

which shows that 17·01 grams of hydrogen peroxide require 8 grams of oxygen, or 1 litre of normal permanganate.

The concentration of commercial hydrogen peroxide may be determined as follows :—Dilute 10 ml. of the solution to 250 ml. in a standard flask. After mixing, measure 25 ml. into a conical flask, and dilute to about 300 ml. Add 25 ml. of dilute sulphuric acid, and titrate with decinormal permanganate.

The commercial practice is to express the concentration of hydrogen peroxide solutions in terms of the volume of oxygen obtainable from them on decomposition by heat. Thus " ten volume " hydrogen peroxide refers to a solution of which 1 ml. will yield 10 ml. of oxygen. It should be observed that the decomposition of hydrogen peroxide by heat,

$$2H_2O_2 = 2H_2O+O_2$$

liberates only half the quantity of oxygen obtainable by oxidation with permanganate.

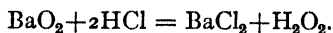
From the result obtained in the titration, calculate the concentration of the original solution (1) as grams per litre of H_2O_2, (2) in terms of the oxygen value, assuming the oxygen to be measured at N.T.P.

If organic preservatives are present, a more accurate result will be obtained by the method on p. 156.

Barium Peroxide.—When barium peroxide is treated with very dilute hydrochloric acid, the hydrogen peroxide formed may be titrated with standard potassium permanganate as in the determination above. The use of sulphuric acid is inadvisable in this case as the barium peroxide may become coated with insoluble sulphate. Hydrochloric acid is permissible, as appreciable amounts of iron are not likely to be present (see p. 121).

Weigh out accurately about 0·2 gram of barium peroxide, and transfer it to a conical flask. Add about 300 ml. of water, and then about 30 ml. of dilute hydrochloric acid. Shake gently until the peroxide is dissolved, and titrate the liberated hydrogen peroxide with decinormal potassium permanganate.

The formation of hydrogen peroxide takes place in accordance with the equation

$$BaO_2+2HCl = BaCl_2+H_2O_2.$$

So that $5BaO_2$ will be equivalent to $2KMnO_4$.

Peroxides of zinc, magnesium, calcium, and sodium, and sodium perborate which also yields hydrogen peroxide on treatment with acids, may be determined by dissolving about one-four hundredth of their equivalent weight in about 100 ml. of *cold* dilute sulphuric acid with continuous stirring. The solution obtained is then titrated with decinormal potassium permanganate.

Dioxides

Manganese Dioxide (Pyrolusite).—The dioxide is boiled with excess of oxalic acid and dilute sulphuric acid until the reaction is complete. Part of the oxalic acid is oxidised by the dioxide and the residual portion is determined by titration with standard permanganate. The equation is

$$MnO_2+H_2C_2O_4+H_2SO_4 = MnSO_4+2H_2O+2CO_2.$$

Prepare an approximately 0·2 normal solution of oxalic acid by dissolving about 3 grams of the crystals in 250 ml. of water. Dilute 10 ml. of this solution to 50 ml., add 25 ml. of dilute sulphuric acid, and titrate (at 70° to 80°) with standard permanganate.

Weigh accurately about 0·4 gram[1] of *finely powdered*[2] pyrolusite in a small weighing tube (small test-tube). Transfer the pyrolusite to a conical flask (about 250 ml.) and reweigh the tube. Measure 50 ml. of the oxalic acid into the flask, add 25 ml. of dilute sulphuric acid, place a small funnel in the mouth of the flask, and boil gently until no black particles remain undissolved. (A small residue of silica is usually present.)

[1] If it is probable that the sample contains less than 75 per cent. of manganese dioxide, a larger quantity should be taken.

[2] It is imperative that the sample be very finely powdered.

Add water to replace that lost by evaporation, and titrate (at 70° to 80°) with standard permanganate.

Calculation.—0·4084 gram of pyrolusite was boiled with 50 ml. of an oxalic acid solution. The residual oxalic acid required 24·60 ml. of 0·1025N permanganate. Also, 10 ml. of the oxalic acid solution required 21·20 ml. of the permanganate, and therefore 50 ml. requires 106·0 ml. Therefore the MnO_2 is equivalent to 106·0−24·60 = 81·40 ml. of 0·1025N permanganate.

From the equation it may be seen that MnO_2 is reduced to manganous sulphate, corresponding to MnO, and 43·46 grams MnO_2 yield 8 grams of oxygen. One ml. of normal permanganate therefore corresponds to 0·04346 gram MnO_2. The percentage of MnO_2 in the sample is therefore

$$\frac{81 \cdot 4 \times 0 \cdot 1025 \times 0 \cdot 04346 \times 100}{0 \cdot 4084} = 88 \cdot 9.$$

Lead Dioxide and Red Lead.—For the determination of lead dioxide by a method similar to that described above for manganese dioxide, the use of sulphuric acid is not satisfactory owing to the insolubility of lead sulphate. If nitric acid is used instead of sulphuric acid, a little oxalic acid may be decomposed by the nitric acid, while the titration of the excess oxalic acid is very slow. The use of perchloric acid avoids these difficulties.

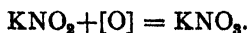
Weigh accurately about 0·3 gram of lead dioxide (PbO_2), or about 0·6 gram of red lead (Pb_3O_4), into a conical flask. Add 25 ml. of 0·2N oxalic acid solution, 100 ml. of 20 per cent. perchloric acid, and heat on a water-bath until the oxide has dissolved. Add 150 ml. of water, heat to 80°, and titrate with standard potassium permanganate.

Nitrite

The oxidation of a nitrite to a nitrate by potassium permanganate in presence of sulphuric acid is shown by the equation

$$5KNO_2 + 2KMnO_4 + 4H_2SO_4 = 5KNO_3 + 2KHSO_4 + 2MnSO_4 + 3H_2O.$$

The oxidation is essentially represented by the equation

$$KNO_2 + [O] = KNO_3.$$

The molar weight (85·1 grams) of potassium nitrite requires 16 grams of oxygen, and therefore 42·6 grams require 1 litre of normal permanganate. The oxidation must be carried out in such a manner as to avoid the loss of nitrous acid that would occur if the nitrite solution were made acid before the permanganate is added.

Procedure.—Prepare a standard (approximately decinormal) solution of oxalic acid by dissolving about 1·5 gram of the crystals in 250 ml. of water and titrating 25 ml. of the solution with decinormal permanganate in the usual way.

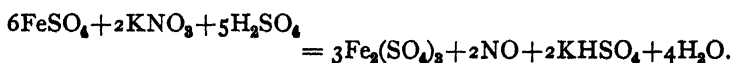
Determine the percentage of potassium nitrite in a sample of the commercial salt. Weigh accurately from 1 to 1·2 gram of the nitrite, dissolve in cold water and dilute to 250 ml. in a standard flask.

Make a preliminary titration of the nitrite solution to find out the approximate amount of potassium permanganate which is required to oxidise a measured volume of it :—Dilute 10 ml. of the nitrite solution to about 100 ml. in a conical flask and warm to about 70°. Add 5 ml. of dilute sulphuric acid and run in standard permanganate until a permanent, decidedly pink, coloration is obtained. Note the volume required. An accurate determination is then made as follows :—

Measure into a conical flask not less than three times the volume of standard permanganate required in the preliminary titration, *i.e.* more than sufficient to oxidise 25 ml. of the nitrite solution. Add 25 ml. of dilute sulphuric acid, dilute to 200 ml., and warm the solution to about 50°. Run 25 ml. of the nitrite solution slowly into the excess of permanganate, with continuous shaking, and then add 10 ml. of concentrated sulphuric acid and heat the mixture to about 80° to complete the oxidation. To the hot solution add (from a burette) a measured excess of standard oxalic acid (sufficient to decolorise the solution), and titrate the excess of oxalic acid with standard permanganate.

Nitrate

When a solution of ferrous sulphate is boiled with a nitrate and excess of sulphuric acid, the ferrous sulphate is oxidised and nitric oxide is set free :

$$6FeSO_4+2KNO_3+5H_2SO_4 = 3Fe_2(SO_4)_3+2NO+2KHSO_4+4H_2O.$$

If, therefore, a known quantity of ferrous sulphate is taken, the amount of nitrate present can be calculated from the amount of ferrous sulphate that becomes oxidised in the process. Air must be carefully excluded during the process, more especially as nitric oxide and oxygen form nitrogen peroxide which would then oxidise more of the ferrous sulphate. The air is accordingly displaced by a current of carbon dioxide. The mixture must contain from 35 to 40 per cent., by volume, of concentrated sulphuric acid.

A

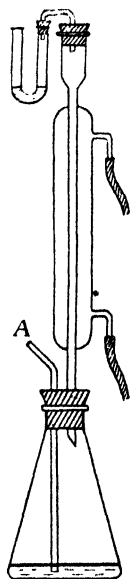



FIG. 33.

The apparatus is shown in Fig. 33. It consists of a 400 ml. conical flask, fitted with a reflux condenser, and provided with a tube A, through which the carbon dioxide enters. A U-tube, containing a little water, is attached to the top of the condenser. The carbon dioxide is supplied from a Kipp generator. If the generator has been freshly charged, the air must be carefully displaced before using the gas.

Procedure.—Prepare a solution of ferrous sulphate by dissolving about 7 grams of the crystals in cold water mixed with 10 ml. of dilute sulphuric acid and dilute the solution to 250 ml. Titrate 25 ml. of the solution with decinormal permanganate.

Weigh accurately 1·2 to 1·3 grams of the nitrate, dissolve in water, and dilute the solution to 500 ml. in a standard flask. Measure 25 ml. of the solution into the conical flask, and add 25 ml. of the ferrous sulphate solution. Connect the flask with the condenser, and pass a rapid current of carbon dioxide through the apparatus for five minutes. Then, without interrupting the current of carbon dioxide, immerse the flask in cold water, remove the U-tube, and slowly introduce, through the condenser, 30 ml. of concentrated sulphuric acid. Replace the U-tube, and reduce the amount of carbon dioxide entering the flask until about one bubble of gas per second passes through the water in the U-tube. Boil the contents of the flask for ten minutes. Increase the rate of the carbon dioxide again, and cool the solution by immersing the flask in water. Detach the flask and rinse the carbon dioxide inlet-tube into it.

Dilute the solution to about 150 ml., and titrate the residual ferrous sulphate with decinormal permanganate.

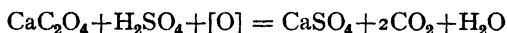
One ml. of normal permanganate corresponds to 0·02834 gram $NaNO_3$.

Exercise.—Determine the percentage of sodium nitrate in a sample of the commercial salt (Chili nitre).

Calcium

The calcium is precipitated as calcium oxalate. The washed precipitate is dissolved in sulphuric acid and the solution is titrated with standard permanganate.

From the equation

$$CaC_2O_4 + H_2SO_4 + [O] = CaSO_4 + 2CO_2 + H_2O$$

it may be seen that the molar weight of CaC_2O_4 (containing 40·08 grams Ca) requires 2 gram-equivalents of oxygen. Therefore 1 ml. of normal permanganate corresponds to 0·02004 gram Ca.

Exercise.—Weigh accurately about 0·15 gram of powdered calcspar. Transfer to a 300 ml. beaker, add 10 ml. of water and 5 ml. of dilute hydrochloric acid, and cover the beaker with a clock-glass. Warm until the calcspar has dissolved, then dilute with a little water and boil the solution for a few minutes in order to free it from carbon dioxide. Rinse the clock-glass into the beaker and add a few drops of methyl red and then ammonia until the solution is neutral. Add 1 ml. of dilute hydrochloric acid, dilute the solution to about 150 ml., heat until boiling, and slowly add a boiling solution of ammonium oxalate. (Use a freshly prepared solution, about 2 per cent.) Now make alkaline with ammonia and boil for a few minutes, stirring in order to avoid " bumping." Allow the precipitate to settle, and then make sure that precipitation is complete by adding a few more drops of the reagent. Place the beaker on the steam-bath for one hour.

Decant the supernatant liquid through a 9-cm. paper, wash the precipitate once by decantation, and then transfer it to the filter (see p. 35). Wash the precipitate and filter paper with water containing a little ammonia (25 ml. of 2N ammonia diluted to 100 ml.), until the washings give no opalescence with nitric acid and silver nitrate. It is better to complete

the washing with a saturated solution of calcium oxalate after most of the ammonium oxalate has been removed. (Always rinse the end of the funnel stem before collecting a portion of the washings—about 5 ml.—for a test like this.)

Now place under the funnel the beaker in which the precipitation was made, pierce the apex of the filter paper with a *pointed* glass rod, and wash the precipitate into the beaker with hot water. Pour about 25 ml. of hot dilute sulphuric acid into the filter, taking care that the acid comes into contact with every part of the paper and that some of it is poured behind the double fold of the paper in case any of the calcium oxalate has lodged there. Then wash the paper thoroughly with hot water. Heat the calcium oxalate solution to about 90°, and titrate with standard permanganate.

Calculate the percentage of calcium in the calcspar.

Lead

The lead is precipitated as lead oxalate by the addition of excess of ammonium oxalate. After making up to a known volume, the ammonium oxalate remaining is titrated in an aliquot portion of the filtrate.

Exercise.—Weigh out accurately about 1·5 gram of lead nitrate, dissolve in water, and make up the solution to 100 ml. Take 25 ml. of this solution in a beaker, and add 50 ml. of an approximately N/10 solution of ammonium oxalate (7·1 grams of $(NH_4)_2C_2O_4, H_2O$ per litre) which has been standardised with a solution of potassium permanganate. Boil for a short time, cool, and transfer to a 100 ml. flask, washing into the flask with successive small amounts of water, and finally making up the volume to 100 ml. Filter through a dry filter into a dry vessel, rejecting the first portions of the filtrate. Titrate 25 ml. of the filtrate with the standard potassium permanganate. Calculate the excess of ammonium oxalate present in the 100 ml. of filtrate, and thence the volume of ammonium oxalate taken to precipitate the lead, and the weight of lead taken for the analysis.

Manganese

The following method is based on the fact that a manganous salt is oxidised to permanganic acid by sodium bismuthate in

presence of acid. The permanganic acid is determined by adding a known excess of ferrous sulphate and titrating the excess with standard permanganate.

Commercial sodium bismuthate is a brown powder of somewhat indefinite composition ; it may be regarded as $NaBiO_3$—a salt of metabismuthic acid, $HBiO_3$.

Very small quantities of manganese can be accurately determined by this method which is particularly well adapted for the determination of manganese in steels, ores, rocks, etc. The solution containing the manganese must be free from chloride ; and the oxidation must be carried out in presence of either nitric acid or sulphuric acid.

The following solutions are required :—

Standard Potassium Permanganate Solution.—Dissolve 0·25 gram of the pure salt in cold water and dilute the solution to 250 ml. One ml. corresponds to 0·0003475 gram Mn. (If the permanganate is of doubtful purity, the solution must be standardised.)

Nitric Acid Solutions.—(*A*) Dilute about 60 ml. of concentrated nitric acid to 250 ml. (*B*) Dilute 8 ml. of concentrated nitric acid to 250 ml. (The concentrated nitric acid should be colourless, *i.e.* free from oxides of nitrogen.)

Sulphuric Acid Solution (3 *per cent.*).—Pour 5 ml. of the concentrated acid into water and dilute the solution to 250 ml.

Ferrous Sulphate Solution.—Dissolve 2·25 grams of $FeSO_4, 7H_2O$ in 125 ml. of 4N sulphuric acid and dilute the solution to 250 ml. The value of this solution in terms of the standard potassium permanganate solution must be ascertained by carrying out a " blank " determination as follows :—Shake together in a flask 50 ml. of nitric acid (*A*) with about 1 gram of sodium bismuthate, add 50 ml. of nitric acid (*B*), and filter through a paper-pulp filter (p. 37).[1] Wash with 50 ml. of nitric acid (*B*). To the filtrate add 25 ml. of ferrous sulphate solution, and titrate at once with the standard permanganate.

Determination of Manganese in Steel.—Weigh accurately

[1] The paper-pulp filter should be washed with a dilute solution of potassium permanganate containing sulphuric acid and then with water. The same pulp may be used for several successive filtrations.

about 1 gram of the steel and transfer it to a 200 ml. conical flask. Add 50 ml. of nitric acid (*A*) and boil gently until the steel is dissolved and the solution free from oxides of nitrogen. Cool, add about 1 gram of sodium bismuthate (in order to oxidise combined carbon), and heat until the pink colour disappears. If manganese dioxide is precipitated, add sufficient sulphurous acid to clear the solution, and then boil for two to three minutes. Cool thoroughly under the tap, or in ice. Add about 2 grams of bismuthate and shake for two minutes. Dilute with 50 ml. of nitric acid (*B*), filter [1] through paper-pulp, and wash with dilute nitric acid (*B*). Add *at once* to the filtrate a measured excess of ferrous sulphate solution (10 ml. to 50 ml. according to the amount of manganese present), and titrate with the standard permanganate without delay.

The percentage of manganese in the sample can then be readily calculated.

Determination of Manganese in Iron Ore.—Take from 0·5 to 2 grams of the ore. Dissolve the weighed portion by warming it in a 200 ml. conical flask (Pyrex glass) with the minimum quantity of concentrated hydrochloric acid—with the addition of a little concentrated nitric acid if organic matter is present. Cool, and add (cautiously) 10 ml. of concentrated sulphuric acid. Manipulate the flask, held in a hand-clamp, over a free flame until all hydrochloric acid is expelled and copious fumes of sulphuric acid are evolved. Allow to cool, dilute with 100 ml. of water, and warm to dissolve the sulphates. Cool, add 2 grams of bismuthate, and shake for at least two minutes. Filter through paper-pulp; rinse the flask and wash the filter with at least 100 ml. of 3 per cent. sulphuric acid. Add to the filtrate (from a weighing-bottle) rather more ferrous ammonium sulphate than is sufficient to decolorise the permanganic acid. (Reweigh the bottle and contents to find the amount added.) Titrate the excess of ferrous salt with the permanganate.

From the data obtained calculate the percentage of manganese in the ore.

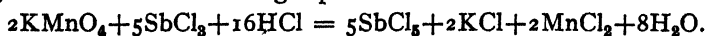
[1] If chromium is present, any delay in filtration may allow oxidation of this to chromate. In the case of high chromium steel, a special method is recommended by Bagshawe (*J. Soc. Chem. Ind.*, 1939, 106T).

Antimony

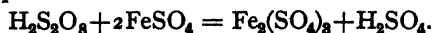
Potassium permanganate oxidises antimonious chloride in presence of hydrochloric acid to antimonic chloride, and antimony in alloys, such as solder, pewter, and type metal, may be determined volumetrically in this way. Tin does not interfere, but if much lead is present, the lead sulphate formed on solution of the alloy in sulphuric acid may retain some antimony which escapes oxidation by permanganate. If arsenic is present it must be removed by volatilisation (see p. 164), or a correction made.

Determination of Antimony in Type Metal.—Weigh accurately about 0·5 gram of the alloy (in fine powder or thin foil). Place it in a 150 ml. round-bottomed flask (Pyrex glass if possible), and add 25 ml. of concentrated sulphuric acid. Heat the mixture, gently at first, and then at the boiling-point of the acid until the alloy is completely disintegrated. It is best to manipulate the flask, held in flask tongs or a hand-clamp, over a free flame. Heating is continued until any undissolved lead sulphate is white or nearly so.

Allow the flask to cool, dilute cautiously with water to 100 ml., and allow the lead sulphate to settle out. Decant the clear liquid into a 400 ml. flask, and boil for five minutes to expel sulphur dioxide. Meanwhile, dissolve the lead sulphate by warming with 20 ml. of concentrated hydrochloric acid and 10 ml. of water. Dilute to 100 ml., and boil out sulphur dioxide. Transfer to a 600 ml. flask, diluting during the process with 250 ml. of water, and titrate with decinormal potassium permanganate at room temperature. Cool the main bulk of the antimony solution, add 20 ml. of concentrated hydrochloric acid and 50 ml. of water. Titrate this with the decinormal permanganate without refilling the burette. From the total volume of permanganate used the antimony can be calculated by means of the following equation :—

$$2KMnO_4+5SbCl_3+16HCl = 5SbCl_5+2KCl+2MnCl_2+8H_2O.$$

Persulphates

Persulphates can be determined indirectly by means of standard permanganate, after previous reduction with excess of ferrous sulphate solution :—

$$H_2S_2O_8+2FeSO_4 = Fe_2(SO_4)_3+H_2SO_4.$$

The excess of ferrous sulphate and thence that oxidised by the persulphate is then determined by means of N/10 potassium permanganate.

Weigh accurately about 0·4 gram of potassium persulphate into a 500 ml. flask, add 50 ml. of N/10 ferrous sulphate solution from a pipette and 50 ml. of 4N sulphuric acid. Then add 200 ml. of hot water that has been boiled for ten minutes to remove dissolved oxygen. After five minutes, cool the flask to room temperature and titrate the excess of ferrous sulphate with N/10 potassium permanganate.

This method is much more satisfactory for the determination of ammonium persulphate than the acidimetric method described on p. 98.

Chromium in Chromium Steel

OUTLINE OF METHOD.—The steel is dissolved in sulphuric acid, the solution oxidised to convert the chromium to chromate, and this is estimated by the addition of standard ferrous salt solution followed by a back-titration with potassium permanganate.

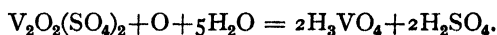
Dissolve 2 grams of the sample in 10 ml. of concentrated sulphuric acid and 60 ml. of water in a 600 ml. conical beaker, and evaporate until fumes of sulphur trioxide are evolved. Cool, and take up in 100 ml. of water. When redissolved, oxidise by adding 3 ml. of concentrated nitric acid, and boil for five minutes. Dilute to 250 ml. with hot water, bring to the boiling-point, and add carefully a 2·5 per cent. solution of potassium permanganate until a very faint permanent precipitate is formed. Add 10 drops of the permanganate solution in excess, and boil for ten minutes. Add a crystal or two of manganous sulphate, and again boil for ten minutes. Cool, and filter through an asbestos pad, washing well with water.

Run in from a burette an excess of decinormal ferrous ammonium sulphate, and titrate back with decinormal potassium permanganate solution until a faint pink colour is obtained. The difference between the ferrous ammonium sulphate solution run in, and that remaining in excess, is equivalent to the chromate formed. From the fact that $6FeSO_4$ is equivalent to $K_2Cr_2O_7$ (p. 118), calculate the percentage of chromium in the chromium steel.

For steels containing less than 0·25 per cent. of chromium, add three or four crystals of potassium permanganate during the solution of the sample. For samples containing more than 10 per cent. chromium, make up the solution to a known volume after filtration and take a suitable fraction for titration.

Vanadium

Vanadium in the form of vanadate can be conveniently determined by reduction of the solution with sulphur dioxide. After removing the excess of sulphur dioxide, the vanadyl salt present is reoxidised to vanadate by standard potassium permanganate.

$$V_2O_2(SO_4)_2+O+5H_2O = 2H_3VO_4+2H_2SO_4.$$

Exercise.—Weigh out accurately about 1 gram of ammonium vanadate, dissolve it in about 75 ml. of hot water, and after cooling make up the solution to 100 ml. Measure out 25 ml. into a conical flask, add 50 ml. of water, and 25 ml. of dilute sulphuric acid. Heat to boiling, and pass sulphur dioxide for two minutes after the colour of solution has become clear blue. Boil off the excess sulphur dioxide, hastening the operation by passing carbon dioxide through the liquid. Cool to 70°, and titrate with decinormal potassium permanganate until a pink tinge persists for thirty seconds.

If the sample of vanadate contains iron, ferrous sulphate will be present in the reduced liquid, and this must first be carefully oxidised, testing for its disappearance by ferricyanide as external indicator.

STANDARD POTASSIUM DICHROMATE

(*N*/10 *solution contains* 4·903 *grams* $K_2Cr_2O_7$ *per litre*)

Dichromate, unlike permanganate, is unaffected by moderate quantities of hydrochloric acid, and it is therefore suitable for the titration of iron when stannous chloride has been used as reducing agent. It has no action on rubber, and may be measured in a burette closed with rubber tubing and a pinch-cock, instead of a glass tap. The solution is quite stable.

As it is not possible to detect a slight excess of potassium dichromate by any change in colour, the end-point of the reaction must be determined by means of (*a*) potassium ferri-

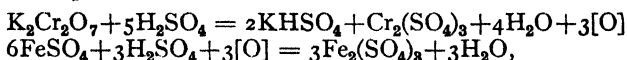
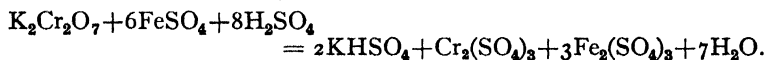
cyanide, which is used as an external indicator, or (*b*) an indicator such as diphenylamine, which is added to the solution which is being titrated. The dichromate must be standardised with the same indicator as that which is subsequently to be used.

Weigh accurately about 4·9 grams of pure potassium dichromate. Transfer to a standard litre flask, dissolve in water, and dilute the solution to 1 litre.

The interaction between potassium dichromate and ferrous sulphate in presence of acid is as follows :—

$$K_2Cr_2O_7+5H_2SO_4 = 2KHSO_4+Cr_2(SO_4)_3+4H_2O+3[O]$$
$$6FeSO_4+3H_2SO_4+3[O] = 3Fe_2(SO_4)_3+3H_2O,$$

or, combining these equations,

$$K_2Cr_2O_7+6FeSO_4+8H_2SO_4 = 2KHSO_4+Cr_2(SO_4)_3+3Fe_2(SO_4)_3+7H_2O.$$

The molar weight of the dichromate thus provides 48 grams (six gram-equivalents) of available oxygen, and a decinormal solution therefore contains one-sixtieth of the molar weight per litre. If the solution is prepared from pure potassium dichromate, the concentration should correspond exactly to the weight of the salt taken. Standard potassium dichromate is used chiefly for the determination of iron, and 1 litre of a decinormal solution will oxidise 5·584 grams.

Titration with Dichromate using Ferricyanide as Indicator.—The solution to be titrated should be placed in a beaker (or conical flask if preferred) and must contain considerable sulphuric or hydrochloric acid ; add, therefore, about 50 ml. of dilute acid, unless the solution is known to contain a corresponding quantity, and then run in the dichromate solution from a burette until all the iron is oxidised.

The potassium ferricyanide solution must be freshly prepared and very dilute (about 0·2 *per cent.), and must contain no ferrocyanide.* To prepare it, take a crystal of potassium ferricyanide weighing slightly more than 0·5 gram, rinse it several times with small quantities of cold water (in order to remove superficial ferrocyanide), and dissolve in 25 ml. of water. Dilute 5 ml. of this solution to 50 ml. The solution decomposes somewhat rapidly, and a fresh one must be made from the solid for each set of titrations.[1]

[1] After a little experience it is easy to prepare a solution of a suitable concentration by carefully rinsing a very small crystal of ferricyanide and dissolving it in a test-tube of water.

The titration is carried out as follows :—Using a small pipette make a series of single drops of ferricyanide solution on a *dry* white tile. Tiles with twelve or more depressions in the surface are convenient for this purpose. Run in the dichromate solution slowly from a burette while swirling the ferrous solution, and from time to time remove a drop of the titrated solution by means of a rod. Add this drop to one of the ferricyanide drops on the white tile, and observe whether a blue colour is produced, which will be the case if any ferrous salt is still present. The rod *must always* be washed by placing it in a large beaker of water before it is returned to the solution being titrated.

When the ferrous iron content of the solution is not known even approximately, time may usually be saved by making a rough titration first, adding the dichromate solution two or more millilitres at a time between each test with ferricyanide solution. A second titration is then carried out without testing with ferricyanide until an amount of potassium dichromate, known from the first titration to be slightly insufficient, has been run in. The end-point is then approached by small additions of dichromate, finally adding single drops.

While the solution still contains an appreciable amount of ferrous salt, a blue coloration is obtained at once with ferricyanide ; but as the amount of ferrous salt diminishes, the blue coloration becomes less apparent, until only a faint blue-green tint is seen. It is only when finally no trace of this develops that no ferrous salt remains and the titration is finished.

Since the blue-green tint develops somewhat slowly near the end it is advisable to allow the test drops on the tile to stand about five minutes before deciding whether the ferrous salt has all been oxidised. Delay on this account can be avoided by proceeding with the titration and writing down the burette readings corresponding to the ferricyanide tests carried out in a definite order on the tile. The required burette reading will of course be that corresponding to the first drop test which shows no blue-green tint after standing five minutes. In this way the end-point can be obtained to one drop or less of dichromate.

In the second titration described above, the error introduced by removing drops of the solution will be very small, because most of the ferrous salt is oxidised before the first drop is removed. The error may be still further reduced by making a

third titration in which the end-point can be approached within 0·25 ml. before testing with the ferricyanide solution.

If the ferricyanide solution contains ferrocyanide, it is impossible to obtain a sharp end-point, since ferric salts give a blue colour with ferrocyanide. For this reason also the ferricyanide must not be exposed to direct sunlight.

Standardisation.—The potassium dichromate solution may be standardised against ferrous ammonium sulphate.

Weigh accurately about 9·8 grams of pure ferrous ammonium sulphate and dissolve this in a small beaker in 125 ml. of 4N sulphuric acid. Transfer this to a 250 ml. standard flask, make up to the mark with water, and mix thoroughly. Measure out 25 ml., add 25 ml. of dilute sulphuric acid and 50 ml. of water, and titrate in the manner described above. Since the concentration of the dichromate solution is approximately known, no drops of the ferrous sulphate solution need be removed until the titration is almost complete.

Titration with Dichromate using Diphenylamine as Indicator.—The use of diphenylamine enables rapid titrations of ferrous solutions to be carried out with potassium dichromate in the presence of chlorides and other substances which react with potassium permanganate.

When treated with various oxidising reagents (*e.g.* nitrates, traces of which may thus be detected), diphenylamine gives a very intense blue colour due to oxidation products, the full depth of which does not in all cases develop immediately.

The concentration of hydrochloric or sulphuric acid in the ferrous solution should be about normal, but may be between 0·5 and 2N. Shortly before the end-point a blue-green colour will develop due to the high ratio of ferric to ferrous iron in the solution, as the former has a slight oxidising action on diphenylamine. The addition of a phosphate or fluoride diminishes this effect owing to the formation of a complex which has a weaker oxidising tendency, and has itself less colour than ferric iron. This point is more fully dealt with on p. 200.

In those cases in which stannous chloride has been used to reduce ferric salts to ferrous (p. 128), the excess of mercuric chloride subsequently added should be kept as small as possible, as this reagent retards the development of the colour. A solution of sodium diphenylamine sulphonate is more satisfactory than diphenylamine if mercuric chloride is present (see p. 128).

Under certain conditions the colour change is reversible, and it is possible to titrate an acid solution of dichromate to which diphenylamine has been added, by means of a ferrous salt.

Standardisation.—Measure out another 25 ml. of the ferrous ammonium sulphate solution used in standardising the potassium dichromate by means of ferricyanide. Add 25 ml. of a mixture of sulphuric and phosphoric acids, made up by adding 10 ml. of concentrated sulphuric acid and 10 ml. of syrupy phosphoric acid to 50 ml. of water and diluting to 100 ml. Then add two drops of a solution of diphenylamine (0·1 gram dissolved in 10 ml. of concentrated sulphuric acid), and run in decinormal dichromate until a greenish-blue colour appears. Continue the addition slowly until an intense violet blue colour is produced.

Standardisation of Potassium Dichromate without using an Indicator

To 25 ml. of the potassium dichromate solution, add 50 ml. of an approximately decinormal solution of ferrous ammonium sulphate in at least 2N sulphuric acid. Titrate the excess of ferrous salt with standard permanganate, taking as the end-point the grey colour produced by the smallest excess of permanganate in conjunction with the green chromic salt. A further 25 ml. of ferrous ammonium sulphate solution is then titrated with the permanganate. The volume of permanganate equivalent to 25 ml. of the dichromate solution can thus be determined.

ANALYSES INVOLVING THE USE OF STANDARD PERMANGANATE OR DICHROMATE SOLUTIONS

Titrations with Permanganate in Presence of Hydrochloric Acid.—The determination of iron by volumetric methods may be made with either a standard permanganate or a standard dichromate solution. If the ferrous salt solution contains no hydrochloric acid, there is little to choose between the two methods in point of accuracy, but the permanganate titration is certainly the more convenient. If the solution contains hydrochloric acid or any chloride, it cannot be accurately

titrated with permanganate unless precautions are taken, because the hydrochloric acid (even when cold and dilute) is oxidised by permanganate in presence of a ferrous salt, and a serious error results. Another source of error is that the end-point of the titration is unsatisfactory on account of the yellow colour of the ferric chloride that is formed.

It is better to avoid a permanganate titration if the ferrous salt solution contains hydrochloric acid, although it is possible to overcome the difficulty almost entirely by adding about 2 grams of hydrated manganese sulphate and 3 ml. of syrupy phosphoric acid. The mixture is then titrated *very slowly* with the permanganate. If any brown or yellow colour is noticed, insufficient phosphoric acid has been added and the titration will be inaccurate.

Iron in Iron Wire

Commercial iron is not chemically pure, although the amount of impurity in some varieties of iron is very small. As determined by volumetric methods, commercial iron sometimes appears to contain more than 100 per cent. of pure iron. This is due to the presence of impurities (carbides, etc.) that have a greater reducing action when dissolved in acid than an equal weight of pure iron.

The determination of the " apparent " percentage of iron in iron wire is made as follows :—Remove any trace of rust from some fine-drawn, soft iron wire (" flower wire ") by means of emery cloth, and then clean the wire with filter paper. Weigh accurately about 1·4 gram of the wire and place it in a 400 ml. flask fitted with a rubber stopper carrying a straight tube of narrow bore (5 mm.) about 50 cm. long. Add 100 ml. of 4N sulphuric acid, and warm the flask gently, preferably on a water-bath, until all the iron has dissolved, and only small particles of carbon remain. Then cool rapidly by gentle rotation in cold water, and make up to 250 ml. in a standard flask, using recently boiled and cooled distilled water. Allow the suspended particles of carbon to settle, and titrate 25 ml. portions of the solution with standard permanganate or dichromate. If permanganate is used, the end-point has been reached when the pink colour persists throughout the solution for a few seconds.

Calculate the percentage of iron in the wire, assuming that the reducing action of the solution is due only to ferrous sulphate.

Iron in Ferrous and Ferric Compounds

If the iron is wholly present in the ferrous condition, it is determined by direct titration with standard permanganate or dichromate, as described under standardisation by means of ferrous ammonium sulphate (pp. 103 and 120).

If the iron is present, wholly or partly, as ferric salt, it must be reduced to the ferrous state before titration. The common methods of reduction are :—

(1) With zinc and acid (this method can only be used in conjunction with permanganate, as zinc salts interfere with the dichromate titration).
(2) With sulphur dioxide.
(3) With hydrogen sulphide.
(4) With stannous chloride.

As the reducing agents themselves also reduce permanganate or dichromate solutions, any excess of the reducing agent must be removed before the titration. If the solution is to be titrated with standard permanganate in the presence of hydrochloric acid or a chloride, phosphoric acid and manganese sulphate must be added (see p. 122).

If titanium is present with the iron it is advisable to use either sulphur dioxide or hydrogen sulphide, as these do not reduce titanic salts.

Exercise.—Determine the percentage of iron in iron alum [ammonium ferric sulphate, $Fe_2(SO_4)_3$, $(NH_4)_2SO_4$, $24H_2O$], using the various methods of reduction described below, and compare the results.

Dissolve about 24 grams (weighed to the nearest centigram) of powdered iron alum in water to which 50 ml. of 4N sulphuric acid has been added. Dilute in a standard flask to 500 ml. and use 25 ml. for each determination.

Reduction with Zinc.—To 25 ml. of the iron alum solution contained in a conical flask, add 25 ml. of water, 10 ml. of concentrated sulphuric acid and 10 grams of "pure," granulated zinc. Two or three drops of copper sulphate solution may be added to hasten the solution of the zinc. Warm *gently*

and allow the reaction to continue until the solution appears quite colourless, and then test for ferric salt :—Place a drop of potassium thiocyanate solution on a white porcelain surface, such as a crucible lid, and then bring into contact with the drop a *trace* of the iron solution which has been withdrawn from the flask by means of a *thin* glass rod or a capillary tube ; a red coloration indicates that reduction has not gone far enough, and this must be continued until the test only produces a faint tinge.

After reduction wait until *almost* the whole of the zinc has disappeared, additional sulphuric acid being added, if necessary, to effect this. (An insoluble residue, chiefly lead, nearly always remains.) Filter through a small plug of glass-wool into a flask containing 25 ml. of dilute sulphuric acid. Rinse the original flask and any undissolved residue several times with dilute sulphuric acid, pouring this also through the filter, and wash the latter carefully with water. Titrate the solution with standard permanganate.

Since the best commercial zinc invariably contains at least a trace of iron, a " blank " determination must be carried out in order to find the correction for that impurity. In the " blank " determination, the same quantities of zinc and sulphuric acid are used but the ferric salt is omitted, and, after the zinc has *almost* completely disappeared, the solution is filtered and titrated with the permanganate. With good zinc, only a few drops of permanganate should be required in the " blank," and an equal amount must be deducted from the volume of permanganate required for the titration of the reduced ferric salt solution.

Reduction with Zinc in a Jones " Reductor."—The reduction of a ferric salt with zinc may be more rapidly accomplished by using a Jones " reductor " (Fig. 34), in which a large surface of zinc is exposed to the solution. The part A to B of the reductor is about 25 cm. long and 2 cm. wide, and is filled with amalgamated zinc granules. The cup C is about 8 cm. long and 4 cm. wide. A tap is provided at T. The reductor is held in a clamp and is fitted into a 400 ml. filter-flask which rests on a block of wood. By taking away the block, the flask can be removed without disturbing the rest of the apparatus.

The amalgamated zinc is prepared as follows :—In a large

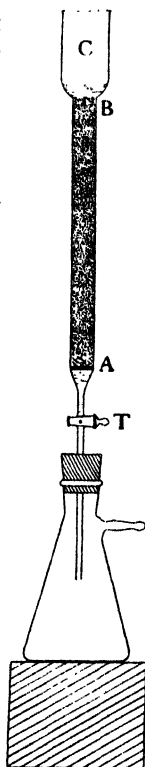
beaker or basin cover 250 grams of zinc granules (sieved through a 10- or 20-mesh screen) with normal hydrochloric acid, stir for a moment, and then add 150 ml. of mercuric chloride solution (0·2N). Stir vigorously until hydrogen ceases to be evolved (about two minutes). Decant the solution and wash the zinc thoroughly by decantation with distilled water. After draining the water as completely as possible, dry the zinc on a clock-glass in the steam-oven.

Place a perforated porcelain disc in the tube at A, and cover this with about 0·3 gram of glass-wool. Then pour into the tube about 30 milligrams of Gooch crucible asbestos mixed with water and drain the water by gentle suction. Fill the part A to B of the tube with the amalgamated zinc.

Prepare approximately 0·2N sulphuric acid by diluting 50 ml. of the dilute acid to 500 ml. Run about 200 ml. of this acid, followed by 100 ml. of water, through the reductor, using gentle suction, keeping the column filled with liquid so that no air can enter. [This precaution must always be observed in using the reductor which should be corked when not in use.] Empty and rinse the filter-flask. The apparatus is now ready for use.

FIG. 34.

"*Blank*" *determination.*—Since the zinc is seldom entirely free from iron, a "blank" determination must be made as follows:—Run 100 ml. of 0·2N sulphuric acid, followed by 100 ml. of water, through the reductor, care being taken to close the tap T before the surface of the zinc is exposed to the air. Detach the flask, add 10 ml. of 4N sulphuric acid, and titrate with standard permanganate. With good zinc only 1 to 2 drops (less than 0·1 ml.) of decinormal permanganate should be required. Repeat the determination to make sure that the "blank" titration requires a constant amount.

Reduction of the ferric salt solution.—Measure 25 ml. of the iron alum solution into a small beaker and add an equal volume of water. (The concentration of acid in this solution is about 0·2N.) Pour the solution into the cup of the reductor,

open the tap, and regulate the suction so that about two minutes are required for the 50 ml. of solution to pass through the column. Close the tap before the zinc is exposed. Rinse the beaker with 50 ml. of 0·2N acid and run this also through the reductor. Finally, rinse the beaker and the cup C with water—using 100 ml. in all—this water also being drawn through the zinc column. Close the tap before the cup is quite empty. Remove the filter-flask, add 10 ml. of 4N sulphuric acid, and titrate the solution with standard permanganate. Deduct the correction indicated in the " blank " determination.

Reduction with Zinc Amalgam.—This is a very satisfactory form in which to use zinc as a reducing agent, and reduction can be effected very rapidly.

The amalgam is prepared by heating 3 to 4 grams of zinc (" free from arsenic ") with 100 grams of mercury and about 20 ml. of dilute sulphuric acid for about an hour in a conical flask on a water-bath. The amalgam is then washed by shaking with water, and filtered through glass-wool from any undissolved zinc. It can be used repeatedly, as no zinc is wasted, hydrogen not being generated in appreciable quantities.

To reduce a solution of ferric alum by means of zinc amalgam, pour 100 grams of the amalgam into a stoppered bottle of about 150 ml. capacity. Add 25 ml. of the decinormal iron alum solution, and 25 ml. of 4N sulphuric acid. Insert the stopper, and shake vigorously for about one minute, when the reduction will be complete. Pour off the colourless solution into a flask, taking care not to allow any of the amalgam to pass over. This is more certainly effected by pouring the reduced solution through a No. 3 sintered glass crucible (p. 214). In carrying out this process, wash the stopper and mouth of the bottle by means of a wash-bottle. Add to the amalgam about 25 ml. of 4N sulphuric acid, insert the stopper and shake. Pour off as before, and repeat the process. This dilute acid is used instead of water for washing, since water gives a turbid liquid which has a slight reducing effect on permanganate.

Titrate the reduced solution in the filter-flask with decinormal permanganate, taking as the end-point the first production of a pink tinge throughout the liquid, though this fades fairly rapidly.

Reduction with Sulphur Dioxide.—If the solution is acid, it must be made nearly neutral by adding ammonia until a

slight permanent precipitate of ferric hydroxide forms. The reducing agent is then added, either in the form of sulphurous acid solution or a sulphite, or by passing a current of sulphur dioxide from a siphon of the liquefied gas through the cold solution. The solution after the reducing agent is added, must be *slightly acid* to litmus; if it is alkaline, no reduction takes place. The excess of sulphur dioxide is removed by adding acid and passing a current of carbon dioxide through the boiling solution.

To 25 ml. of the iron alum solution, add ammonia until a slight permanent precipitate forms, and then 25 ml. of sulphurous acid solution. Boil the mixture for ten minutes. Now add about 20 ml. of dilute sulphuric acid, heat to boiling again, and pass a fairly rapid current of carbon dioxide through the boiling solution until the sulphur dioxide is completely expelled (about twenty minutes). Cool the solution—without interrupting the gas current—by placing the flask in a basin of water. Rinse the gas-delivery tube and remove it. Titrate the solution with either standard permanganate or dichromate.

Reduction with Hydrogen Sulphide.—By passing a current of hydrogen sulphide through a solution of a ferric salt, sulphur is precipitated and the ferric salt is completely reduced to the ferrous state. The solution should contain about 2 per cent. by volume of concentrated sulphuric acid. The excess of hydrogen sulphide is removed by passing a current of carbon dioxide through the boiling solution.

Add 10 ml. of dilute sulphuric acid to 25 ml. of the iron alum solution contained in a 200 ml. flask. Dilute to about 50 ml., pass hydrogen sulphide into the cold solution for at least fifteen minutes, then heat until boiling, and continue the current of gas until the precipitated sulphur has coagulated. Allow the solution to cool somewhat without interrupting the gas current, and then filter into another flask, rinsing the original flask and washing the filter carefully. Dilute the solution, if necessary, to about 100 ml., and pass a fairly rapid current of carbon dioxide through the boiling solution until hydrogen sulphide cannot be detected in the escaping gas by means of lead acetate paper.[1] Cool the solution—without interrupting

[1] Ten minutes is usually sufficient. If the solution is milky (on account of sulphur in suspension) a minute trace of hydrogen sulphide, which may be neglected, will always be found in the escaping gas.

the gas current—and titrate it with standard permanganate or dichromate.

The acidity of a ferric solution which is to be reduced by hydrogen sulphide should be between 0·4N and 0·5N. Phosphoric acid must not be present.

Reduction with Stannous Chloride.—Stannous chloride is added to the ferric salt solution containing hydrochloric acid until the colour is discharged. The excess of the stannous chloride is destroyed by adding mercuric chloride, and the solution is then titrated with standard dichromate.

The stannous chloride solution may be prepared by dissolving 3 grams of $SnCl_2, 2H_2O$ in 25 ml. of concentrated hydrochloric acid, and diluting to about 100 ml.[1]

To 25 ml. of the iron alum solution (p. 123) contained in a 300 ml. flask, add 5 ml. of concentrated hydrochloric acid, heat until boiling, and then run in the stannous chloride drop by drop from a burette until the yellow colour of the solution is just discharged. A slight excess (one or two drops) of the stannous chloride is essential, but a large excess must be carefully avoided. *Cool the solution* in the flask,[2] dilute to 150 ml., and add (rapidly, and while stirring) about 10 ml.[3] of saturated mercuric chloride solution. A very slight, *white* precipitate should form. If no precipitate appears, insufficient stannous chloride has been added, whilst a grey or black precipitate shows that too much stannous chloride was used; in either case the experiment must be rejected.

Titrate the turbid mixture with standard dichromate, or add phosphoric acid (see p. 122) and titrate with permanganate. If standard potassium dichromate is used, either potassium ferricyanide may be used as an external indicator, or a solution of sodium diphenylamine sulphonate as internal indicator, this being less affected by excess of mercuric chloride than is diphenylamine.

Sodium diphenylamine sulphonate is prepared by stirring 0·32 gram of barium diphenylamine sulphonate into 90 ml. of water, and adding 0·5 gram of sodium sulphate in 10 ml. of water.

[1] The side-shelf reagent is suitable, if it has been recently prepared.

[2] This may be done conveniently by covering the mouth of the flask by a small inverted beaker, and placing under the tap.

[3] If diphenylamine is to be used as an indicator, not more than 3 ml. of mercuric chloride must be added.

After stirring the mixture for some time, filter off the precipitate. Six to eight drops of the filtrate are used for each titration, 25 ml. of a mixture of sulphuric and phosphoric acids (p. 121) being added to remove the ferric ions as they are formed. The end-point is shown by a change from the green colour of the chromic ion to a bluish grey.

Total Iron in a Mineral

(*Hæmatite; Magnetite; Bog Iron Ore; etc.*)

If the ore is in large pieces, a representative sample is crushed (without grinding) in a clean, steel percussion mortar. The coarse powder is then finely ground in an agate mortar. Iron ores sometimes dissolve very slowly in acid unless they are reduced to an impalpable powder.

Dissolving the Ore.—Weigh accurately about 1 gram of the ore, or a larger quantity if the ore contains but little iron. If the ore contains carbonaceous matter (as is often the case), weigh it in a porcelain crucible, and heat to dull redness for ten minutes.

Transfer the weighed portion of the ore, after ignition, to a 200 ml. flask, and add 15 ml. of concentrated hydrochloric acid. Warm on the steam-bath for some time, and then keep near the boiling-point of the acid until the undissolved residue, if any, is perfectly white. (Nothing is gained by boiling vigorously—this merely weakens the acid.)

If after half an hour the residue is still coloured, add to the hot liquid at intervals 1 to 2 ml. of stannous chloride (avoiding excess); rapid solution usually follows in the case of a hæmatite ore. If excess of stannous chloride is inadvertently added, add potassium permanganate until the yellow colour due to ferric iron returns.

When as much as possible of the ore has been brought into solution, and whether the residue is coloured or not, dilute with a little water, and filter into a 100 ml. standard flask. Rinse the original flask and wash the filter carefully, first with dilute hydrochloric acid and then with water, using as little as possible. If the filtrate contains all the iron, cool and make it up to 100 ml.

If the insoluble residue is coloured, therefore probably

containing iron (provided organic matter was destroyed by ignition), incinerate the filter paper together with the residue in a porcelain crucible (p. 218). Then add 2 to 3 grams of previously fused potassium hydrogen sulphate (pyrosulphate), heat cautiously, and keep the mixture fused until the dark specks of iron oxide have disappeared. Cool, place the crucible in a small porcelain basin, and dissolve the solid residue in the minimum quantity of dilute sulphuric acid. Filter if necessary (most of the silica remains undissolved), and receive the filtrate and rinsings in the flask containing the main solution of the ore. Dilute to 100 ml.

Titration of the Solution.—Use 25 ml. of the solution for each titration. If stannous chloride was used in the preparation of the solution, the reduction of the ferric salt must also be effected with stannous chloride; otherwise hydrogen sulphide or sulphur dioxide may be used as the reducing agent. After reduction, the solution may be titrated with either standard dichromate or permanganate. If standard permanganate is to be used, phosphoric acid and manganese sulphate must be added before the titration (p. 122).

Methods for Refractory Oxides and Silicates.—The acid treatment described above will not always dissolve all the iron in the sample. The addition, from time to time, of a few crystals of potassium chlorate to the concentrated hydrochloric acid promotes the solution of refractory oxide such as magnetite. The same treatment also serves to oxidise any sulphides or carbonaceous matter the sample may contain. If potassium chlorate has been added, the solution should then be boiled for some time, or evaporated to a small volume, in order to free it from chlorine.

Natural silicates and artificial siliceous slags must be decomposed, as a rule, by fusing with sodium carbonate, or "fusion mixture," as described under silica (p. 341). If only the iron in the silicate is to be determined, it is not necessary to evaporate to dryness in order to remove the silica. The acid solution obtained after the fusion is treated as follows:—Warm the solution in a beaker, add a little bromine water and heat until boiling, in order to oxidise any ferrous salt. Precipitate the iron (together with aluminium, manganese, etc.) by adding ammonia in slight excess. Boil for a minute, allow the precipitate to settle, filter, transfer the precipitate to the

filter, and wash it thoroughly with hot water. Place the funnel in a flask, and dissolve the precipitate on the filter by pouring through the funnel a hot mixture of 10 ml. of concentrated hydrochloric acid and 10 ml. of water. Wash the filter carefully, at first with hot dilute hydrochloric acid and then with hot water. Reduce with stannous chloride, and titrate with standard potassium dichromate.

Separate Determination of Ferrous and Ferric Iron in a Mineral

Ferrous Iron.—The exact determination of ferrous iron in minerals is a very difficult operation. Reference may be made to Hillebrand's *Analysis of Silicate and Carbonate Rocks* for a description of the methods employed and the difficulties encountered.

Certain precautions are necessary in regard to the grinding, as it is found that considerable oxidation occurs if the sample is ground to a fine powder in the ordinary manner. A very fine powder is usually essential, and oxidation may be prevented by grinding *the weighed sample* under alcohol in an agate mortar. The alcohol is then allowed to evaporate spontaneously.

Solution must then be effected in absence of air. If the mineral dissolves in hydrochloric acid, the operation may be conducted in a flask which has been filled with carbon dioxide before the acid is added, and which is kept filled by passing a current of carbon dioxide into the flask until solution is complete. The solution is then cooled in an atmosphere of carbon dioxide, diluted if necessary, and titrated with standard potassium dichromate.

If the mineral does not dissolve readily in hydrochloric acid, it must be decomposed in absence of air by means of hydrofluoric acid in presence of sulphuric acid. (For details, see Hillebrand, *loc. cit.*)

Ferric Iron.—The total iron is then determined by one of the methods already described, and the difference between the total iron and the ferrous iron gives the amount present in the ferric state.

Iron in Ink

Inks often owe their colour to iron-tannin compounds. The organic matter must be destroyed before the iron in the ink can be determined.

Weigh (to the nearest centigram) 10 grams of ink in a 100 ml. porcelain basin. Evaporate to dryness on the steam-bath, and then heat the residue and burn away the organic matter at as low a temperature as possible. Dissolve the ash by warming with about 10 ml. of concentrated hydrochloric acid, adding, if necessary, a few drops of stannous chloride at intervals. Transfer the solution to a 300 ml. flask, reduce with stannous chloride and titrate with standard dichromate as described on p. 128.

Express the result in grams of Fe_2O_3 per 100 grams of ink.

Iron and Chromium in Chrome Iron Ore

Decomposition of the Ore.—Grind the ore *very finely* in an agate mortar. Weigh accurately about 0·5 gram, transfer to a nickel crucible, and mix thoroughly by means of a thin glass rod with 5 to 6 grams of sodium peroxide. Heat the crucible gently with a very small Bunsen flame until the contents melt, and then keep the mixture at low redness for about ten minutes. Remove the flame until a crust forms, then add another gram of sodium peroxide, and heat again to low redness for about five minutes.

Place the crucible, after cooling, in a porcelain basin, add about 50 ml. of water, and warm until the yellow mass has dissolved. Remove the crucible and rinse it. If the solution is purple in colour, add a little more sodium peroxide, and then boil the solution in the covered basin until the excess of sodium peroxide is *completely* decomposed. In order to destroy the large excess of sodium hydroxide in the solution, add about 5 grams of ammonium carbonate and boil again. Filter and wash the precipitate thoroughly. Determine the iron in the precipitate and the chromium in the filtrate.

Iron.—Dissolve the precipitate by pouring hot hydrochloric acid (equal volumes of concentrated acid and water) into the filter, and receive the solution in a 300 ml. conical flask. Wash the filter with hot dilute hydrochloric acid and then with hot

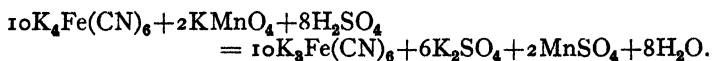
water. (If any dark-coloured residue remains, it must be fused again with sodium peroxide.) Reduce the ferric salt in the solution with stannous chloride, and titrate with standard dichromate (p. 128).

Chromium.—Add 4N sulphuric acid to the filtrate until it is acid (orange-yellow), and then add 25 ml more acid. Allow the solution to cool; then reduce the dichromate by adding a known excess of ferrous ammonium sulphate, as follows:—Place several grams of the powdered ferrous salt in a weighing-bottle and weigh the bottle and contents; then add the salt to the chromate solution gradually, while swirling, until it is free from orange-yellow colour, and until a small drop of the solution gives a blue coloration with a drop of freshly prepared potassium ferricyanide solution.

Titrate the excess of ferrous salt in the solution with standard dichromate. Also weigh the weighing-bottle again, and thus determine the weight of ferrous ammonium sulphate used.

Ferrocyanides

Ferrocyanides can be titrated directly in acid solution by means of potassium permanganate, but it is not easy in this case to see a slight excess of this reagent. This difficulty can be avoided by adding excess of permanganate to the acidified ferrocyanide solution, and determining the excess by running in decinormal ferrocyanide, after the addition of a few drops of ferric sulphate solution, until a permanent bluish-green colour is obtained. So long as any permanganate remains in solution, the standard ferrocyanide added is at once oxidised to ferricyanide, which does not give a blue colour with a ferric salt.

$$10K_4Fe(CN)_6 + 2KMnO_4 + 8H_2SO_4 = 10K_3Fe(CN)_6 + 6K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Exercise.—Prepare 100 ml. of decinormal potassium ferrocyanide by dissolving 4·223 grams of the pure crystallised salt, $K_4Fe(CN)_6, 3H_2O$, in water and making up to 100 ml. Measure out 10 ml. of bench ferrocyanide solution, add about 60 ml. of dilute sulphuric acid, and run in decinormal permanganate from a burette until the liquid has a definitely red tinge. Add a few drops of a solution of ferric alum, and run in the decinormal potassium ferrocyanide with constant shaking until

the solution acquires a bluish-green tint throughout. Calculate the normality of the bench ferrocyanide.

STANDARD CERIC SULPHATE

(*N/10 solution contains* 33·23 *grams* $Ce(SO_4)_2$ *per litre*)

Cerium forms two series of salts, cerous and ceric, in which it is trivalent and tetravalent respectively. Cerous salts are colourless, and can be oxidised to ceric salts, which are yellow or orange, by oxidising agents such as persulphates and sodium bismuthate. Ceric salts are reduced by ferrous salts, oxalates, nitrites, etc.

As an oxidising agent in volumetric analysis, ceric sulphate possesses the following advantages. It cannot be reduced below the cerous state, its titre remains constant for long periods in light and air, and it is less affected by the presence of hydrochloric acid than is potassium permanganate. When used for the oxidation of a colourless solution, the presence of a slight excess of ceric sulphate is detectable by its colour, though the change is less marked than when potassium permanganate is used. In the case of coloured solutions, however, an indicator is necessary to show the end-point of the reaction. There are several such indicators available. They are organic compounds, the oxidation products of which differ in colour from that of the reduced form. A fuller discussion of these indicators will be found on p. 200. As in the case of potassium permanganate, titrations are usually carried out in the presence of sulphuric acid.

The equivalent weight of pure crystalline ceric sulphate, $Ce(SO_4)_2, 4H_2O$, is 404·3, but the commercial salt contains impurities. An approximately decinormal solution of ceric sulphate is prepared by adding 14 grams of the salt to 200 ml. of 2N sulphuric acid, and heating until the liquid is almost clear. Cool, and filter into a 250 ml. flask, and dilute to the mark.

The ceric sulphate solution must now be standardised by means of sodium oxalate, which is oxidised in acid solution in accordance with the equation

$$H_2C_2O_4 + 2Ce(SO_4)_2 = Ce_2(SO_4)_3 + H_2SO_4 + 2CO_2.$$

Weigh out accurately about 0·18 gram of sodium oxalate,

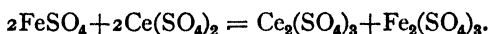
which has been previously dried at 120°. Dissolve this in about 200 ml. of water, add 5 ml. of concentrated sulphuric acid, and heat nearly to boiling. Now run in the ceric sulphate solution until a very faint permanent yellow tint is obtained. One drop in excess should be sufficient to show the colour change, but it is advisable to run a "blank" titration, using the same volume of hot acidified liquid containing no oxalate. The volume of ceric sulphate required for this blank titration should be deducted. Repeat the titration with another weighed portion of the sodium oxalate.

Oxalic Acid and Oxalates

The procedure is described above under the standardisation of ceric sulphate with sodium oxalate.

Iron

Iron must be present in the ferrous state, and if necessary the solution must first be reduced, preferably by zinc (p. 123). The equation for the reaction is

$$2FeSO_4+2Ce(SO_4)_2 = Ce_2(SO_4)_3+Fe_2(SO_4)_3.$$

Since ferric sulphate has a slight colour, an indicator must be used to determine the end-point of the titration. Various indicators may be used for this purpose, the most satisfactory being *o*-phenanthroline; but N. phenylanthranilic acid, which is less expensive, may usually be substituted.

The *o*-phenanthroline indicator is prepared as follows:—Make up 7 ml. of a 0·025M ferrous sulphate solution by dissolving 0·05 gram of $FeSO_4,7H_2O$ in 7 ml. of dilute sulphuric acid. Add 0·1 gram of *o*-phenanthroline (p. 201), and shake until all the solid is dissolved. One drop of this solution should be used for each titration. The change at the end-point is from red to almost colourless.

If N. phenylanthranilic acid is to be used as indicator, prepare a 0·005M solution of its sodium salt by dissolving 0·106 gram in a little water containing about 0·05 gram of sodium carbonate, and diluting to 100 ml. About four drops of this solution are used for titration. The colourless solution goes pink at the end-point. Since the redox potential (p. 201) is 1·08 volt, the addition of a phosphate is unnecessary.

If neither of these indicators is available, the titration may be carried out with diphenylamine or sodium diphenylamine sulphonate as indicator. These, however, are less satisfactory, since they tend to decompose in the presence of ceric sulphate. The details of their use are given on pp. 120 and 128.

Procedure.—Weigh out accurately about 1 gram of ferrous ammonium sulphate, dissolve it in a mixture of 50 ml. of dilute sulphuric acid and 50 ml. of water. Add the appropriate amount of indicator, and titrate with standard ceric sulphate.

One ml. of N/10 ceric sulphate corresponds to 0·005584 gram of iron.

Iodides

This determination depends upon the liberation of iodine, each atom of which displaces one atom of hydrogen from acetone which is present in excess. Mono-iodo-acetone is formed.

$$KI + 2Ce(SO_4)_2 + C_3H_6O = KHSO_4 + Ce_2(SO_4)_3 + C_3H_5IO.$$

It will be seen that, owing to the displacement by the iodine of an equivalent amount of hydrogen in an ionic form from the acetone, the equivalent weight of potassium iodide for this reaction is half its molecular weight.

Procedure.—Make up 100 ml. of M/20 potassium iodide solution by dissolving 0·830 gram of potassium iodide in water. Measure out 25 ml. of this solution into a 500 ml. flask, add 25 ml. of acetone, 35 ml. of dilute sulphuric acid, and dilute to about 100 ml. Add one drop of *o*-phenanthroline ferrous sulphate (see the determination of Iron above), and titrate with standard ceric sulphate solution until the red colour changes to a very pale blue. A brown colour due to free iodine may develop in the liquid if the addition of the ceric sulphate is rapid, and the liquid must be stirred until this disappears before proceeding. The vapour of mono-iodo-acetone has an irritant effect on the eyes.

Ferrocyanides

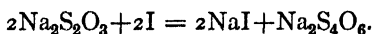
Ceric sulphate oxidises ferrocyanides to ferricyanides according to the equation

$$2K_4Fe(CN)_6 + 2Ce(SO_4)_2 = 2K_3Fe(CN)_6 + Ce_2(SO_4)_3 + K_2SO_4.$$

Make up an approximately decinormal solution of potassium ferrocyanide by dissolving 4·2 grams of the crystalline salt in water, and diluting to 100 ml. Measure out 25 ml. of this solution into a 600 ml. flask, add 250 ml. of water, and two drops of a solution of diphenylamine prepared by dissolving 0·1 gram in 10 ml. of concentrated sulphuric acid. Titrate with standard ceric sulphate until a deep blue colour is produced.

Standard Sodium Thiosulphate and Standard Iodine

SODIUM thiosulphate is useful in volumetric analysis mainly on account of the manner in which it interacts with iodine, viz. :—

$$2Na_2S_2O_3+2I = 2NaI+Na_2S_4O_6.$$

The process may be used for the determination of iodine itself and all substances (mainly oxidising agents) that will liberate iodine from potassium iodide, and is therefore capable of wide application.

Standard iodine solution is used as an oxidising agent for the determination of easily oxidisable substances, such as sulphurous acid, arsenic (as sodium arsenite), and tin (as stannous chloride). Sometimes the standard iodine and thiosulphate solutions are used in conjunction.

In iodometric titrations an excess of potassium iodide must always be present to prevent any volatilisation of iodine, and the titration should be carried out in a flask. A dilute solution of starch is generally used as an indicator. This is a very sensitive reagent for minute traces of iodine, provided that a soluble iodide is present.

In cases where it is necessary to add acid to liberate iodine the hydrion concentration must not be too high. Otherwise the free hydriodic acid formed is liable to liberate additional iodine owing to atmospheric oxidation. Acetic acid may always be used with safety, but the concentration of a mineral acid should not exceed 0·25 normal except in the absence of oxygen.

STANDARD SODIUM THIOSULPHATE

(*N*/10 *solution contains* 24·82 *grams of* $Na_2S_2O_3$, $5H_2O$ *per litre*)

Since the molar weight (248·2 grams) of sodium thiosulphate, $Na_2S_2O_3$, $5H_2O$, is equivalent to 126·9 grams of iodine (see the above equation), a solution that contains 24·82

grams of the salt per litre is described as a decinormal solution. The so-called "pea-crystals" of photographic "hypo" are usually very pure, but when the salt is dissolved in ordinary distilled water it suffers slight decomposition and the concentration of the solution slowly alters, possibly owing to the action of bacteria. It is a common practice to add a small amount of sodium carbonate or borax to preserve the solution. Recent work shows that the addition of either of these substances is undesirable. One objection is that the resulting solution is found to have a slightly different normality when it is used for titrating a standard substance in acid solution from that obtained when it is used in titrating the same or another standard substance in neutral solution. A litre of approximately decinormal solution which keeps well can be prepared by adding about 25 grams of pure sodium thiosulphate to about 950 ml. of water at the boiling-point, boiling for a few minutes, cooling, and making up to a litre with recently boiled and cooled water. Kassner and Kassner [*Ind. Eng. Chem. Anal.* Edn., 1940, p. 655] recommend the addition of 0·4 ml. of chloroform per litre as a preservative. This may be used in a solution prepared with water which has not been boiled, or as an additional precaution in a solution prepared as described above. The solution is standardised as described below. It should be kept in the dark, or the stock bottle covered with brown paper to exclude light.

Preparation of the Starch-Indicator Solution.—Mix 1 gram of "soluble starch" with a little cold water, pour the mixture into 200 ml. of almost boiling water, and boil for about one minute. After cooling, the solution is ready for use. If "soluble starch" is not available, grind 1 gram of ordinary starch with a little cold water, pour the mixture slowly into 200 ml. of boiling water and boil for two minutes. Set aside for a few hours (or overnight) and decant the clear liquid. Starch solution will not keep in good condition for more than about two days unless it is sterilised, *e.g.* by adding either 5 ml. of dilute hydrochloric acid or 2 milligrams of mercuric chloride or iodide to the above quantity.

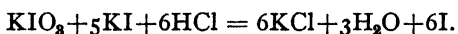
Standardisation of Sodium Thiosulphate with Pure Iodine. —Commercial iodine is often impure, and should be ground up with a little solid potassium iodide and resublimed before

use.[1] On account of its volatility, iodine cannot be accurately weighed in the ordinary manner; and the following special method must therefore be adopted.

In a weighing-bottle place about 2 grams of pure potassium iodide with 10 *drops* of water. Allow to rise to room temperature, wipe the outside dry, and weigh accurately. Add 0·3 to 0·4 gram of pure iodine, replace the stopper at once, and weigh again. This gives the weight of the iodine. When the iodine has dissolved, wash it rapidly into a flask containing about 1 gram of potassium iodide in about 200 ml. of water, and titrate *at once* with the sodium thiosulphate solution. When the iodine solution becomes very pale yellow in colour, add about 2 ml. of starch solution and continue the titration until the blue colour just disappears. Repeat the process with another weighed quantity of iodine and from the results calculate the normality of the thiosulphate solution.

The starch solution must not be added until near the end of the titration. If the volume of the iodine solution is not large, it is possible to complete the titration without using starch—except in artificial light.

Standardisation of Sodium Thiosulphate with Potassium Iodate.—Potassium iodate is easily obtained in a pure state, and may be used in standardising sodium thiosulphate. It is used in presence of an excess of potassium iodide and dilute hydrochloric acid, when the following reaction takes place :

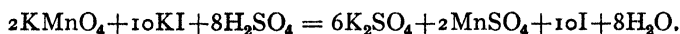
$$KIO_3 + 5KI + 6HCl = 6KCl + 3H_2O + 6I.$$

The equivalent weight of potassium iodate is therefore one-sixth of its molecular weight.

Dry a few grams of potassium iodate at 120°, and prepare 250 ml. of a decinormal solution by dissolving 0·8918 gram in water, and making up in a graduated flask. To 25 ml. of water in a flask add 2 grams of potassium iodide, 0·5 gram of sodium bicarbonate, and 10 ml. of dilute hydrochloric acid.

[1] A small quantity of pure iodine may be prepared as follows :—Grind together in a mortar about 2 grams of iodine with about 0·2 gram of potassium iodide. Place the mixture in a small porcelain basin, cover with a round-bottomed flask containing cold water, and heat gently, so that the iodine sublimes slowly on to the flask. The iodine must then be dried by enclosing it in a narrow stoppered weighing-tube containing a little calcium chloride covered with a layer of glass-wool.

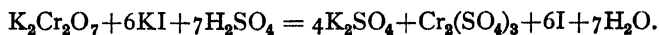
Run in 25 ml. of the iodate solution, and titrate the liberated iodine with the thiosulphate solution.

Standardisation of Sodium Thiosulphate with Potassium Permanganate.—If potassium permanganate is added to an acid solution of potassium iodide, the permanganate is reduced and an equivalent amount of iodine is liberated. A solution of sodium thiosulphate can therefore be standardised by titrating the iodine liberated from potassium iodide by a measured volume of standard potassium permanganate solution.

$$2KMnO_4+10KI+8H_2SO_4 = 6K_2SO_4+2MnSO_4+10I+8H_2O.$$

Dissolve about 2 grams of potassium iodide in 50 ml. of water in a 400 ml. flask, add 10 ml. of dilute sulphuric acid, about 0·5 gram of sodium bicarbonate, and 25 ml. of standard (decinormal) potassium permanganate. Allow to stand in the dark for five minutes, dilute to about 200 ml., and titrate the liberated iodine with the thiosulphate solution as described above.

A " blank " titration should be carried out using the same quantities of potassium iodide and sulphuric acid, and the thiosulphate reading subtracted from that obtained before.

Standardisation of Sodium Thiosulphate with Potassium Dichromate.—When potassium dichromate is added to an acid solution of potassium iodide, iodine is liberated according to the equation

$$K_2Cr_2O_7+6KI+7H_2SO_4 = 4K_2SO_4+Cr_2(SO_4)_3+6I+7H_2O.$$

If a standard (decinormal) solution of potassium dichromate is available, it may be used for the standardisation of the thiosulphate solution, the procedure being the same as with standard permanganate (see above). Instead of a standard solution, weighed quantities of potassium dichromate may be used. The method tends to give results that are slightly too high.

Dissolve about 2 grams of potassium iodide in 50 ml. of water, add 10 ml. of dilute sulphuric acid and about 0·5 gram of sodium bicarbonate. To this solution add 0·12 to 0·14 gram (accurately weighed) of potassium dichromate and allow to stand for five minutes in the dark. Then dilute to about 200 ml., and titrate the liberated iodine with the thiosulphate solution, using starch as indicator. At the conclusion of this titration the solution is green in colour, on account of the chromic sulphate

present. The colour change at the end-point—from blue to light green—is nevertheless easily observed if the solution is diluted to at least 200 ml.

The gram-equivalent of potassium dichromate is 49·03.

Standardisation of Sodium Thiosulphate with Pure Copper. —This is described on p. 145.

STANDARD IODINE

(*N*/10 *solution contains* 12·69 *grams per litre*)

Iodine is almost insoluble in water, but dissolves in a solution of potassium iodide. It is very volatile, and in both the preparation and use of a standard iodine solution, precautions are necessary to prevent loss by volatilisation. Commercial iodine is usually impure, and, even if pure iodine is available, it is difficult (on account of its volatility) to prepare an accurate standard solution by weight. It is preferable, therefore, to prepare an approximately decinormal solution from commercial (B.P.) iodine, and standardise it with a standard sodium thiosulphate solution, or by means of arsenious oxide or barium thiosulphate.

On a rough balance weigh 6·4 grams of powdered iodine and introduce it into a 500 ml. standard flask. Add 10 to 12 grams of potassium iodide (free from iodate), and *not more than* 20 *ml. of water*. Shake until all the iodine has dissolved, and then dilute to the graduation mark. Iodine dissolves quickly in a concentrated potassium iodide solution, but very slowly in a dilute solution, and much time will therefore be wasted if the solution is diluted before all the iodine has dissolved.

Standardisation with Arsenious Oxide.—The oxidation of arsenious oxide by iodine may be represented by the equation

$$As_2O_3 + 4I + 2H_2O \rightleftharpoons 4HI + As_2O_5.$$

The reaction is reversible, but the oxidation is quantitative if the hydriodic acid is neutralised as it is formed. Neither sodium hydroxide nor sodium carbonate may be used for this purpose, since they interact with iodine, but sodium bicarbonate introduces no appreciable error if the solution is saturated with carbon dioxide. The hydrolysis of the bicarbonate is then very slight, and the solution at the end of the titration is approximately neutral.

Measure out from a burette (owing to the poisonous properties of the solution) 25 ml. of standard arsenious acid solution prepared as described on p. 159, into a conical flask. Add 2 ml. of starch solution, and 15 ml. of a saturated solution of sodium bicarbonate (prepared in the cold). Run in iodine solution slowly from another burette until a permanent blue tint is just obtained throughout the solution.

The gram-equivalent of arsenious oxide is 49·45.

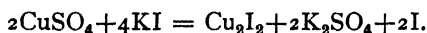
Standardisation with Barium Thiosulphate.—Weigh out accurately about 0·7 gram of BaS_2O_3, H_2O into a beaker, and add about 100 ml. of water. Run in the iodine solution slowly with continuous stirring. When most of the sparingly soluble barium salt has reacted, add starch solution and complete the titration.

The gram-equivalent of barium thiosulphate is 267·5.

ANALYSES INVOLVING THE USE OF STANDARD IODINE AND STANDARD THIOSULPHATE

Copper

When a copper salt is mixed with a solution of potassium iodide, cuprous iodide is precipitated and iodine is liberated :

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + 2I.$$

The amount of copper can therefore be found by titration of the free iodine. According to the equation, 1 gram of copper requires 5·22 grams of potassium iodide, but in practice a considerable excess of the latter is necessary; if the solution to be titrated contains about 0·15 gram of copper—requiring about 25 ml. of standard (decinormal) thiosulphate—about 2 grams of potassium iodide should be added.

Arsenic, antimonic, and ferric compounds may interfere in this titration unless special precautions are taken. [*Ind. Eng. Chem. Anal.* Edn., 1936, viii. 119.]

Exercise.—The copper in a bronze coin, or in brass, may be determined by this method.

Clean a halfpenny with emery cloth, and cut it into four approximately equal pieces. Weigh one of the pieces accurately. Place the weighed piece in a 200 ml. conical flask, add 5 ml. of water and 5 ml. of concentrated nitric acid, and warm on

the steam-bath until the alloy has dissolved (about twenty minutes). The small white residue of stannic oxide need not be filtered off, since it in no way interferes with the analysis.

It is essential that the solution to be titrated should contain no nitrite, and the following procedure must be closely adhered to. Dilute the solution with 25 ml. of water and boil it briskly for two minutes in order to expel oxides of nitrogen. Rinse the neck and side of the flask with a little water, and then add about 0·5 gram of urea [1] (in order to destroy traces of nitrous acid). Neutralise the nitric acid by adding ammonia (about 15 ml.) until a bluish-white precipitate forms. Then add dilute acetic acid (about 5 ml.) more than sufficient to redissolve the precipitate. Cool, and dilute the solution to 250 ml. in a standard flask.

In a 200 ml. conical flask, dissolve 2 grams of potassium iodide in 20 ml. of water, and add 25 ml. of the copper solution. (Cuprous iodide is nearly white, but the free iodine colours the mixture brown.) Titrate the mixture with standard sodium thiosulphate until the brown colour becomes faint; then add 2 ml. of starch solution, and continue the titration until the mixture loses the last trace of a grey-blue tinge and appears almost white. In case traces of iodine have been adsorbed by the precipitate, it is advisable at this point to add about a gram of potassium thiocyanate, and if the blue colour returns, discharge this by further addition of a drop or so of thiosulphate. The end-point is quite sharply defined. After reading the burette, however, it will be found advantageous—until some experience has been gained—to add a few additional drops of the thiosulphate and to keep the mixture as a guide for a second titration.

The rapid reappearance of the blue colour soon after the titration is apparently finished indicates that the solution has not been completely freed from nitrite, and the determination will therefore be inaccurate.

Calculate the percentage of copper in the coin. One litre of normal thiosulphate corresponds to 63·57 grams of copper.

Standardisation of Sodium Thiosulphate with Pure Copper.

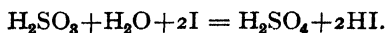
[1] Instead of urea, bromine-water may be added until the solution shows a slightly greenish tint. The excess of bromine is then removed by boiling until the issuing steam no longer produces a blue colour with potassium iodide-starch paper.

—If a solution of sodium thiosulphate is to be used mainly for the determination of copper, it is best to standardise it in the following manner :—Weigh accurately about 0·15 gram of pure (electrolytic) copper foil. Place it in a 200 ml. conical flask, add 1 ml. of water and 1 ml. of concentrated nitric acid, and warm the flask on the steam-bath until the copper has dissolved. Following the method detailed above, dilute the solution with 25 ml. of water, boil briskly for two minutes, and add 0·5 gram of urea (see footnote, p. 144). Then add ammonia until a precipitate forms, and redissolve the precipitate in dilute acetic acid. Cool, add 2 grams of potassium iodide, and titrate the mixture with the thiosulphate as described above.

Alternative Method.—Weigh accurately about 2·5 grams of pure copper sulphate. Wash it into a 100 ml. standard flask and dissolve in water. Add about 1 ml. of dilute ammonia and 5 ml. of dilute acetic acid, and dilute the solution to the mark. Measure 25 ml. of the solution into a conical flask, add 2 grams of potassium iodide, and titrate with the thiosulphate solution. (One litre of normal thiosulphate corresponds to 249·7 grams of $CuSO_4, 5H_2O$.)

Sulphurous Acid and Sulphites

Sulphurous acid in dilute aqueous solution is oxidised by iodine to sulphuric acid according to the equation

$$H_2SO_3 + H_2O + 2I = H_2SO_4 + 2HI.$$

The alkali sulphites are oxidised to sulphates in a similar manner. The sulphite solution is run into a measured excess of acidified iodine solution (not *vice versa*), with constant stirring, and the residual iodine is then titrated with standard thiosulphate. If the iodine is run into the sulphite solution, the reaction takes place in accordance with the above equation only when the sulphite solution is very dilute (about centinormal).

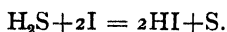
Exercise.—Determine the percentage of Na_2SO_3 in a sample of commercial sodium sulphite crystals. Weigh accurately from 2·5 to 2·8 grams of the crystals, dissolve in water, and dilute to 250 ml. in a standard flask.

Measure 25 ml. of decinormal iodine into a flask, add 5 ml. of dilute hydrochloric acid, dilute to about 100 ml., and add

slowly 25 ml. of the sulphite solution. Titrate the excess of iodine with standard thiosulphate.

Hydrogen Sulphide

Hydrogen sulphide interacts with iodine in aqueous solution according to the equation

$$H_2S+2I = 2HI+S.$$

A measured volume of the hydrogen sulphide solution is run into excess of decinormal iodine, and the excess of the latter is then titrated with standard thiosulphate.

If the concentration of the hydrogen sulphide solution is more than about 0·025 normal, the precipitated sulphur encloses a portion of the iodine which is thereby protected from interaction with the thiosulphate; the titration is then inaccurate. Accordingly, after making a preliminary titration, the hydrogen sulphide solution must be diluted in a standard flask *with air-free water* in such proportions that 10 ml. of decinormal iodine will oxidise about 40 ml. of the sulphide solution.

Hydrogen Sulphide in Mineral Water.—In order to determine the amount of hydrogen sulphide in mineral waters, take a measured volume, say 5 ml. of decinormal (or centinormal) iodine, add starch solution and 2 grams of potassium iodide, and pour in the water from a measuring cylinder until the blue colour is discharged. Titrate back with decinormal (or centinormal) iodine. A correction is necessary for the amount of iodine required to produce a blue colour in absence of hydrogen sulphide. In order to determine this, add starch solution and 2 grams of potassium iodide to a quantity of distilled water equal in volume to that of the mineral water used, and titrate with the iodine.

Exercise.—Determine the normality of a solution of hydrogen sulphide prepared by passing a slow stream of fine bubbles of the gas through water at room temperature for ten minutes. Measure out this solution from a burette.

Mercurous Mercury and Ferric Iron

Mercury can be determined when in the form of mercurous nitrate by means of standard iodine, and a standard solution

of this salt may be used for the determination of iron in the ferric state (Bradbury and Edwards, *J.S.C.I.*, 1940, 96T).

Determination of Mercurous Mercury.—The mercurous solution is run into a measured volume of standard iodine which oxidises it to the mercuric state, red mercuric iodide being precipitated. Sufficient potassium iodide is added near the end-point to dissolve the mercuric iodide, and the titration is finished, adding starch solution when the colour is pale yellow. If the potassium iodide is added at the beginning of the titration, considerably more of the mercurous solution will have to be added before all the free iodine has been removed. It is advisable, however, to make a preliminary titration in which the potassium iodide is added at first in order to determine at what stage of the subsequent accurate titration the potassium iodide should be added. The final disappearance of the starch iodide colour is somewhat slow, passing through a bluish-green stage and it is therefore better not to add the starch solution until practically all the free iodine has gone. If too little potassium iodide is added, a slight yellow suspension appears near the end-point. This does not appreciably affect the result, but makes it more difficult to decide when the starch solution should be added.

Make up 250 ml. of an approximately N/10 solution of mercurous nitrate by dissolving about 7·3 grams of the salt (which usually contains mercuric nitrate) in a solution of nitric acid containing 13 ml. of the concentrated acid previously diluted to 250 ml., and after the solid has dissolved, make the solution up to 250 ml. with the above acid, and mix.

Make a preliminary titration by measuring out 25 ml. of N/10 iodine into a small flask. Add 20 ml. of a solution containing 10 grams of potassium iodide in 100 ml. of solution, and run in the mercurous nitrate with continuous shaking until the yellow colour of the free iodine just disappears. It is unnecessary to add starch solution, as the end-point will be incorrect and about 1 ml. too high. Note the volume of the mercurous solution required.

Now make an accurate titration by measuring out another 25 ml. of N/10 iodine into the same flask, and with constant shaking run in the mercurous solution until within 3 ml. of the reading in the preliminary titration. To the red suspension of mercuric iodide add 20 ml. of the above potassium iodide

solution and shake until the precipitate has completely dissolved. The solution should now be clear and contain a slight excess of iodine. The excess of iodine is then removed by further cautious addition of mercurous nitrate, shaking continuously and adding starch solution when the iodine colour has become quite pale. The final bluish-green colour should be discharged by one drop of the mercurous solution, allowing a short time after thorough mixing. Repeat the titration on another 25 ml. of iodine solution, and calculate the normality of the solution of mercurous nitrate. One litre of decinormal mercurous nitrate contains 20·06 grams of mercury.

Ferric Iron by Standard Mercurous Nitrate.—The reduction of a solution of ferric iron by mercurous nitrate in presence of a thiocyanate affords a convenient and a direct method for the determination of iron in the ferric state. If the iron is partly present in the ferrous state, this can be first titrated by potassium permanganate and the total iron then determined by mercurous nitrate. The chief advantage of the method lies in the much greater stability of mercurous nitrate as compared with that of the titanous salt solutions usually employed in a direct titration of ferric iron. Ammonium thiocyanate is used as indicator, and it is essential that not less than about 10 equivalents of this salt be present for each equivalent of iron. If less than this minimum proportion is used, a heavy precipitate forms and the red colour of ferric thiocyanate remains after the theoretical amount of mercurous nitrate has been added. An excess of thiocyanate is not harmful. The presence of dilute sulphuric acid does not interfere with the end-point, but the presence of hydrochloric acid necessitates the addition of slightly more than the theoretical amount of mercurous nitrate. If, however, the final concentration of hydrochloric acid is not greater than about 0·2N the error is not more than 0·5 per cent.

Measure out 25 ml. of an approximately N/10 solution of ferric alum (see p. 123) into a 200 ml. stoppered bottle, and add 25 ml. of a solution of ammonium thiocyanate containing 20 grams in 100 ml. of solution. Run in mercurous nitrate solution while continually swirling the liquid in the bottle until the colour becomes noticeably weaker. After this stage add the mercurous nitrate solution, a drop or two at a time, insert the stopper, and shake after each addition. A single drop will

discharge the last tinge of red, but there should not be much delay in finishing the titration, as there is a tendency for the red colour to return. Repeat the titration on another 25 ml. of the ferric alum solution.

Dioxides, Chromates, Chlorates, etc.

Substances that oxidise hydrochloric acid with evolution of chlorine may be accurately determined in the following manner. The method is specially useful for dioxides such as lead dioxide, red lead, and manganese dioxide, and as an illustration the determination of manganese dioxide in pyrolusite is described.

Valuation of Pyrolusite.—Manganese dioxide interacts with hydrochloric acid according to the equation

$$MnO_2+4HCl = MnCl_2+2H_2O+Cl_2.$$

If the chlorine is passed into potassium iodide solution, it liberates an equivalent amount of iodine which may be determined by titration with standard sodium thiosulphate solution.

Reduce some pyrolusite to a fine powder by thorough grinding. In a small weighing-tube (1 cm. wide and 2 cm. long) weigh accurately from 0·10 to 0·15 gram of the powder, and introduce the tube and contents into a 200 ml. distillation flask (Fig. 35).

Fit the flask with a cork and glass tube, so arranged that a current of carbon dioxide from a Kipp apparatus can be passed into the flask and through the solution that is to be boiled in it. Connect the bent side-tube of the flask with a U-tube which contains 2 grams of potassium iodide dissolved in just sufficient water to fill the bend of the tube. As a precaution against incomplete absorption, connect with the U-tube a tube full of glass beads wetted with potassium iodide solution. Place the U-tube in a basin of cold water.

When the apparatus is ready, pour 10 ml. of water and 20 ml. of concentrated hydrochloric acid into the flask, and replace the cork at once. Heat the mixture very gently, so that chlorine is slowly evolved. Gradually increase the temperature and finally heat until boiling, and pass a slow current of carbon dioxide through the boiling solution until all the chlorine is driven out of the flask (about ten minutes as a rule). In order to prevent the iodine and potassium iodide solution from passing

back into the flask, increase the current of carbon dioxide immediately the heating is stopped. (As pyrolusite invariably

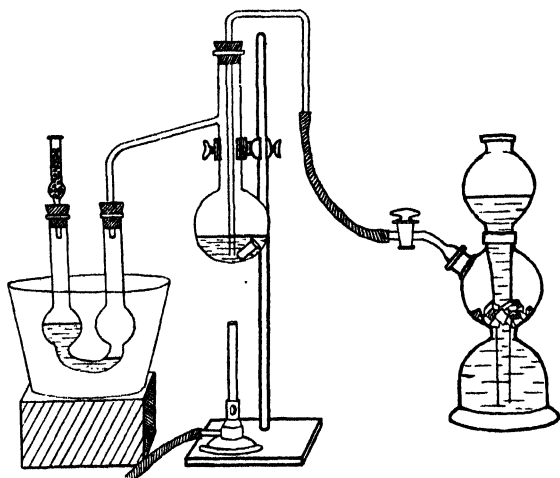



FIG. 35.

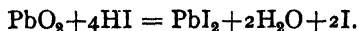
contains iron, the solution in the flask remains yellow at the end of the operation.)

Disconnect the absorption tube, wash the iodine and potassium iodide solution into a flask, and titrate at once in the usual manner with sodium thiosulphate.

Calculate the percentage of MnO_2 in the sample.

Lead Dioxide and Red Lead

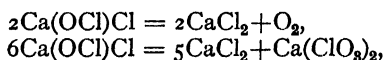
The lead dioxide is mixed with a solution containing hydrochloric acid, potassium iodide, and a large excess of sodium chloride. The lead dioxide is converted into lead iodide which dissolves in the excess of sodium chloride, and an equivalent amount of iodine is liberated :

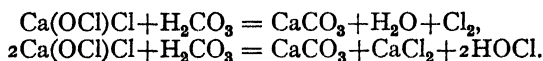
$$PbO_2+4HI = PbI_2+2H_2O+2I.$$

Place in a 200 ml. stoppered bottle 100 ml. of water, 20 ml. of concentrated hydrochloric acid, 1 gram of potassium iodide, and 20 to 25 grams of sodium chloride. Add 0·25 gram of *finely powdered* lead dioxide and shake vigorously for about two minutes. Titrate the liberated iodine with decinormal thiosulphate. Calculate the percentage of PbO_2 in the sample.

This method can also be used for red lead; 0.7 gram should be taken.

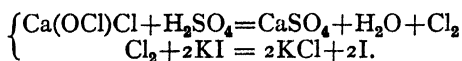
Available Chlorine in Bleaching-Powder

Bleaching-powder may be regarded as a mixed salt, $Ca(OCl)Cl, H_2O$. When treated with acid, the whole of the chlorine in this mixed salt, amounting to about 49 per cent., is liberated, and is therefore "available." The best commercial samples, however, seldom contain more than 36 to 38 per cent. of available chlorine. Bleaching-powder decomposes slowly on keeping, with formation of calcium chloride and chlorate:

$$2Ca(OCl)Cl = 2CaCl_2 + O_2,$$
$$6Ca(OCl)Cl = 5CaCl_2 + Ca(ClO_3)_2,$$

whilst exposure to atmospheric moisture and carbon dioxide results in loss of chlorine and hypochlorous acid:

$$Ca(OCl)Cl + H_2CO_3 = CaCO_3 + H_2O + Cl_2,$$
$$2Ca(OCl)Cl + H_2CO_3 = CaCO_3 + CaCl_2 + 2HOCl.$$

The available chlorine thus diminishes on keeping, and is no longer equal to the total chlorine (see p. 180).

The amount of available chlorine may be determined by mixing a solution of the bleaching-powder with excess of potassium iodide and adding acid. The reaction is:

$$\begin{cases} Ca(OCl)Cl + H_2SO_4 = CaSO_4 + H_2O + Cl_2 \\ Cl_2 + 2KI = 2KCl + 2I. \end{cases}$$

The liberated iodine, which is equivalent to the available chlorine, is then titrated with standard thiosulphate. The procedure is as follows:—

Weigh accurately (in a stoppered weighing-bottle) about 2·5 grams of bleaching-powder. Bleaching-powder is not completely soluble in water; in order to obtain a uniform sample, it must be so finely ground that the insoluble portion will remain for some time in suspension. Transfer the weighed sample to a glazed porcelain mortar, add 2 to 3 ml. of water, and grind to a smooth paste. Add more water gradually, then transfer the mixture completely to a 250 ml. standard flask and make up to the mark. Mix the contents of the flask by shaking, and repeat the shaking immediately before withdrawing each sample for titration.

Measure 25 ml. of the mixture into a 200 ml. flask, add about 1 gram of potassium iodide (10 ml. of a 10 per cent. solution), and excess of dilute acetic acid. Titrate the iodine with standard thiosulphate.

Alternative Method.—The available chlorine in bleaching-powder may also be determined by means of standard arsenious acid (see p. 159).

Total Arsenic in Commercial Arsenious Oxide

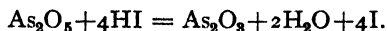
Commercial arsenious oxide often contains some arsenic oxide as impurity. The following method of analysis is applicable also to mixtures of arsenious and arsenic salts.

Determination of Arsenious Oxide.—The arsenious oxide may be determined by the process already described for standardising a solution of iodine by means of arsenious acid (p. 142).

Weigh accurately about 1·2 gram of a sample of the commercial oxide. Dissolve in 10 ml. of warm sodium hydroxide solution, add 20 ml. of dilute hydrochloric acid, and make the solution up to 250 ml. in a standard flask.

Measure from a burette 25 ml. of the solution into a conical flask, add 10 ml. of a saturated solution of sodium bicarbonate, and titrate with decinormal iodine solution, using starch as indicator (p. 143).

Determination of Arsenic Oxide.—In strongly acid solution, arsenic acid is reduced by hydriodic acid to arsenious acid with liberation of iodine :

$$As_2O_5+4HI = As_2O_3+2H_2O+4I.$$

The reaction is complete within a few minutes if the solution is very strongly acid.

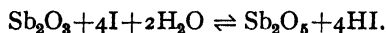
Evaporate 50 ml. of the arsenic solution (measured from a burette) until the volume is reduced to about 5 ml., cool, and pour into a 200 ml. conical flask. Do not rinse the basin with water. Prepare a solution of hydriodic acid by dissolving 2 grams of potassium iodide in 10 ml. of water and adding 10 ml. of concentrated hydrochloric acid (free from chlorine). Rinse the basin into the flask with this solution without delay.

Cover the flask with a watch-glass, and set aside for at least ten minutes. Then dilute to about 50 ml., and titrate

the liberated iodine with decinormal sodium thiosulphate *without* using starch indicator.

Antimony

Antimonious oxide interacts with iodine in the same way as arsenious oxide, and antimony may be determined by titration with a standard iodine solution in similar manner :

$$Sb_2O_3+4I+2H_2O \rightleftharpoons Sb_2O_5+4HI.$$

The hydriodic acid formed in the reaction must be neutralised by means of sodium bicarbonate as in the case of arsenic. In order to prevent precipitation of the antimony when an acid solution is diluted or neutralised, tartaric acid is added.

Antimony in Tartar Emetic.—Weigh accurately about 4 grams of tartar emetic and dissolve it in about 100 ml. of hot water. As the salt is a tartrate, the addition of further tartaric acid is unnecessary. Cool the solution and dilute it to 250 ml. in a standard flask. Measure 25 ml. into a conical flask, add 10 ml. of a saturated solution of sodium bicarbonate, and titrate with decinormal iodine. Run the iodine solution down the side of the flask in order to avoid loss of carbon dioxide (p. 143), and use starch indicator as usual.

Antimony in Antimony Oxide.—Weigh accurately about 1·8 gram of antimony oxide. Dissolve the oxide by warming in a beaker with 5 ml. of concentrated hydrochloric acid, and then add about 5 grams of tartaric acid dissolved in a little water. Transfer the solution and the rinsings of the beaker to a 250 ml. standard flask, cool, and dilute to the graduation mark. Measure 25 ml. of the solution into a conical flask, add 25 ml. of a saturated solution of sodium bicarbonate, and titrate with decinormal iodine as described under tartaric emetic.

In case the sample contains antimonic oxide, reduce the antimonic to antimonious chloride in another portion of the solution by adding about 1 gram of sodium sulphite (or by passing sulphur dioxide through the warm solution). Boil the solution gently for five minutes and then pass a current of carbon dioxide through the boiling solution until the sulphur dioxide is expelled. Cool the solution, add 25 ml. of sodium bicarbonate solution, and titrate with decinormal iodine.

Tin in an Alloy

Preparation of a Solution for Analysis.—Dissolve a weighed portion of the alloy (from 0·1 to 1 gram, according to the amount of tin) in concentrated hydrochloric acid with careful exclusion of air. This simple method, which dispenses with further reduction, is possible with some alloys such as solders and pewters, and is described on p. 370.

If the alloy is not completely soluble in hydrochloric acid alone, place it in a small flask on the steam-bath with 25 ml. of the acid and add about 0·5 ml. of bromine, or a few crystals of potassium chlorate, from time to time. When completely dissolved, support the flask in a water-bath at 65° to 70°, and pass a current of carbon dioxide or air through the solution until bromine or chlorine ceases to be evolved. It is advisable that the temperature should not exceed 70° during the passage of the gas, or stannic chloride may be lost by volatilisation.

If the alloy cannot be brought into solution by the above method, disintegrate it with nitric acid as described on p. 372, dilute to about 30 ml., filter, and wash the residue with hot water. Analyse the residue by the method given for an ore (p. 155), or for tin in bronze (p. 372).

Reduction and Titration.—The tin is reduced to the stannous condition by warming the solution containing hydrochloric acid with metallic iron or nickel, or by boiling it with metallic antimony. The stannous chloride is then determined by titration with standard iodine solution.

Stannous chloride is very readily oxidised by atmospheric oxygen, and it is essential, therefore, that the solution should be protected from contact with the air both before and during the titration. This is accomplished by keeping the flask filled with carbon dioxide.

Procedure.—(*a*) If copper, arsenic, or antimony is present, place the solution, diluted to 100 ml. and containing 25 per cent. by volume of concentrated hydrochloric acid, in a 300 ml. beaker. Place a clean iron rod or a coil of piano wire in the solution, cover with a clock-glass, and keep near the boiling-point for about thirty minutes or until the solution becomes colourless. (Copper, arsenic, and antimony are precipitated, and tin is for the most part reduced to stannous chloride.)

Remove and rinse the iron, filter the solution into a 400 ml. flask, and proceed at once as described in (*b*).

(*b*) If copper, arsenic, and antimony are absent (or have been removed), place the solution in a 400 ml. flask fitted with a rubber stopper carrying a bent inlet tube for carbon dioxide, and a straight, wide tube, about 7·5 cm. by 8 mm. Add 50 ml. of concentrated hydrochloric acid and about 1 gram of antimony powder (*free from sulphide*), and dilute to 200 ml.

Pass a slow current of carbon dioxide through the flask, while heating on the water-bath for twenty minutes, and then boiling briskly for five minutes. Cool the solution by placing the flask in cold water, while passing a *rapid* current of carbon dioxide through the flask. When cold, add starch solution and titrate with decinormal iodine. Run in the iodine solution through the straight tube without lifting the rubber stopper, and maintain a current of carbon dioxide through the flask during the titration.

The end-point in the titration is attained when a blue coloration persists throughout the solution. The blue coloration may subsequently disappear on account of further reduction by the antimony, but this occurs so slowly, in the cold, that it does not interfere with the titration.

Tin in an Ore

Preparation of a Solution for Analysis.—Fuse about 8 grams of potassium hydroxide in a spun iron crucible, and continue the heating until all moisture is expelled and quiet fusion attained. Cool, add about 0·5 gram (accurately weighed) of the finely powdered ore, cover the crucible, and heat, at first cautiously, and then with a full Bunsen flame until action ceases. Pour the molten mass into a clean nickel basin floating in a dish of water, and cover the hot mass with a crucible lid to prevent loss when the mass cracks during cooling.

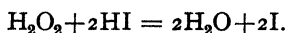
Place the iron crucible in a porcelain basin, add 100 ml. of water, and boil. If any of the fused mass remains attached to the crucible, add a little hydrochloric acid, and assist the solution process by breaking off any adhering lumps with a glass rod. When the crucible is clean, remove and rinse it. To the solution add the detached cake, together with the crucible lid if there is anything attached to it. Add 30 ml. of concentrated

hydrochloric acid and heat on a water-bath. There should be no undissolved residue from the ore, but there may be a few scales of ferric oxide from the crucible.

Transfer to a 400 ml. conical flask, add 30 ml. of concentrated hydrochloric acid, dilute to about 200 ml. with hot water, and proceed at once with the reduction and titration as described on p. 154.

Hydrogen Peroxide

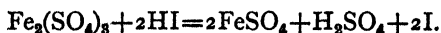
Hydrogen peroxide slowly oxidises a solution of hydriodic acid, and may therefore be determined by titration of the iodine liberated :

$$H_2O_2+2HI = 2H_2O+2I.$$

This method is better than that described on p. 106, as the presence of organic compounds, often added to stabilise hydrogen peroxide, will lead to results which are too high if the permanganate method is used.

The hydrogen peroxide must be diluted in a standard flask until it is not more than 0·3 normal. Ten ml. of this solution are added with constant shaking to a solution of 2 grams of potassium iodide and 2 grams of sodium bicarbonate in 200 ml. of dilute sulphuric acid in a conical flask. After allowing the mixture to stand five to ten minutes, the liberated iodine is titrated with thiosulphate, adding starch when the colour of the iodine has been nearly discharged.

Iron

Ferric salts may be determined without previous reduction, since in acid solution they liberate iodine on addition of potassium iodide, and this can be titrated with thiosulphate solution.

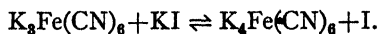
$$Fe_2(SO_4)_3+2HI=2FeSO_4+H_2SO_4+2I.$$

The reaction is slow at ordinary temperatures, but it can be accelerated by the addition of a catalyst such as cuprous chloride or by heating. Heating would involve loss of iodine unless carried out in a closed vessel, but if the iodine which is liberated on standing for a few minutes at ordinary temperatures is first removed by running in thiosulphate, and the solu-

tion is then heated to 50° C. there is no appreciable loss of the small amount of iodine subsequently liberated. It is, however, necessary to displace the air in the titration flask by carbon dioxide to avoid high results, as an appreciable amount of iodine is set free by atmospheric oxygen, probably owing to oxidation of the ferrous salt formed. Sodium bicarbonate is therefore added to the acid solution.

Weigh out accurately about 4 grams of powdered ferric alum, and dissolve this in about 40 ml. of water containing 15 ml. of dilute sulphuric acid, and make up to 100 ml. in a graduated flask. Measure out 25 ml. of this solution into a 250 ml. flask, add 10 ml. of dilute sulphuric acid (hydrochloric acid may be used if free from dissolved chlorine), and dilute to about 60 ml. Now add 1 gram of sodium bicarbonate, which will neutralise only part of the free acid, and 2 grams of potassium iodide, and at once fit a cork loosely into the flask or plug with cotton-wool. Keep the flask in the dark for five minutes and then run in 0·1N thiosulphate until the free iodine has just disappeared, but do not add starch yet. Heat the solution to about 50° C. with the flask still loosely corked, and complete the titration, finally using starch solution.

Ferricyanides

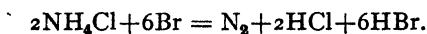
Soluble ferricyanides react incompletely with potassium iodide, the following equilibrium being established :—

$$K_3Fe(CN)_6 + KI \rightleftharpoons K_4Fe(CN)_6 + I.$$

This reaction goes completely to the right if excess of zinc sulphate is added to precipitate the ferrocyanide as it is formed. The free iodine can be titrated with thiosulphate.

Exercise.—Weigh out accurately about 0·6 gram of potassium ferricyanide, and dissolve it in 50 ml. of water in a conical flask. Add 10 ml. of dilute hydrochloric acid, and about 2·5 grams of potassium iodide and 0·5 gram of sodium bicarbonate. When these have dissolved, add 2 to 3 grams of zinc sulphate (free from iron), shake well and allow to stand for two minutes. Titrate the liberated iodine by means of thiosulphate, using starch as indicator.

Ammonium Salts by Bromine-Water

Ammonium salts may be rapidly determined by means of their interaction with bromine-water (Levy, *Z. Anal. Chem.*, 1931, vol. 84, p. 98), if the acidity is correctly adjusted by the addition of sodium bicarbonate. The reaction is as follows :—

$$2NH_4Cl + 6Br = N_2 + 2HCl + 6HBr.$$

Excess of bromine-water is added, and the amount unused determined by titrating the iodine liberated by it from a solution of potassium iodide.

Procedure.—Determine the strength of a stock bromine-water roughly by adding 5 ml., from a burette or small measuring cylinder, to a solution of 2 grams of potassium iodide in water acidified with 5 ml. of dilute hydrochloric acid. Titrate the iodine liberated with a standard sodium thiosulphate solution (see p. 140). Make up in a stoppered flask 250 ml. of approximately 0·05 normal bromine-water by appropriate dilution of the stock. Loss of bromine from the solution during the subsequent titrations may be diminished by the addition of 5 to 10 grams of potassium bromide during dilution, but if care is exercised this precaution is not essential. Standardise the prepared bromine-water accurately by running 50 ml. from a burette into acidified potassium iodide solution, and titrating with thiosulphate.

Weigh out accurately about 0·5 gram of ammonium chloride, dissolve, and make up to 100 ml. in a standard flask. To 10 ml. of this solution in a conical flask add 50 ml. of water, and 3 grams of sodium bicarbonate. Run in bromine-water from the burette, while shaking until a definite yellow tint due to excess of bromine is observed. Allow to stand for a few minutes. Add 2 grams of potassium iodide, and make the solution definitely acid with dilute hydrochloric acid, adding this carefully through a funnel in the mouth of the flask, the outside of the funnel being washed down into the flask after the evolution of carbon dioxide has ceased. Titrate the liberated iodine with sodium thiosulphate, and thence calculate the weight of bromine which was used in the reaction with ammonium chloride. From this the weight of ammonium chloride present may be found, remembering that, from the equation, 3Br is equivalent to NH_4.

STANDARD ARSENIOUS ACID

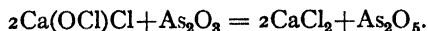
(*N*/10 *solution contains* 4·945 *grams* As_2O_3 *per litre*)

Standard arsenious acid is used as a reducing agent for the determination of available chlorine in bleaching-powder, hypochlorites, iodine, etc. It may also be used for standardising potassium bromate and potassium permanganate. It is prepared from arsenious oxide which, unless known to be pure, must be purified as follows :—Dissolve 10 grams of the commercial oxide in 50 ml. of warm concentrated hydrochloric acid. Add 100 ml. of water and set the solution aside overnight. Filter the crystals of arsenious oxide that separate, wash them with a little cold water, and dry in a desiccator.

Weigh accurately in a small porcelain basin about 1·25 gram of pure arsenious oxide. Add 10 ml. of sodium hydroxide solution (bench reagent) and warm the basin on the steam-bath, stirring the mixture gently, until the oxide dissolves (about five minutes). Transfer the solution and the rinsings of the basin to a 250 ml. standard flask. Add enough dilute hydrochloric acid to make the solution acid to phenolphthalein and dilute the solution to the graduation mark.

Available Chlorine in Bleaching-Powder

This method depends on the oxidation of trivalent arsenic to the pentavalent state by the hypochlorite. The reaction may be represented by the following (simplified) equation :—

$$2Ca(OCl)Cl + As_2O_3 = 2CaCl_2 + As_2O_5.$$

Standard arsenious acid solution (see above) is run into the bleaching-powder solution from a burette, and the end of the reaction is determined by means of potassium iodide-starch paper ; so long as any hypochlorite remains undecomposed, a blue stain is produced on the test-paper when a drop of the solution is brought into contact with it. The procedure is as follows :—

Prepare a solution of the bleaching-powder in the manner described on p. 151. After shaking, measure 25 ml. of the turbid mixture into a small beaker and make a rough titration by running in the standard arsenious acid, rapidly at first,

and then 0·5 ml. at a time, stirring constantly, until a drop of the solution gives no blue stain when placed on potassium iodide-starch paper.

Repeat the titration, only on this occasion remove no test drops until within about 1 ml. of the previously determined end-point. As the end-point is approached, the blue stain becomes less pronounced, and is last seen near the centre of the wet spot on the test-paper. The end-point is quite sharp.

Calculate the percentage of available chlorine in the bleaching-powder.

Preparation of Potassium Iodide-Starch Paper.—Grind 0·5 gram of starch with a little cold water, pour into 100 ml. of boiling water, boil for a minute, and cool. Add about 2 ml. of 10 per cent. potassium iodide solution. Dip strips of filter paper into the mixture and hang them over a glass rod until dry. Preserve the strips in a stoppered bottle.

STANDARD TITANOUS SULPHATE

(*N/10 solution contains* 19·20 *grams of* $Ti_2(SO_4)_3$ *per litre*)

Titanous salts are powerful reducing agents which may be used to determine a variety of substances, organic as well as inorganic, by volumetric methods. In presence of acid they reduce ferric salts to ferrous salts, chromates to chromic salts, and chlorates to chlorides ; in alkaline solution nitrates are reduced to ammonia. Organic nitro-compounds, such as nitro-benzene and picric acid, are reduced to the corresponding amines ; azo-compounds and dyestuffs like indigo are reduced and decolorised.

Many applications of titanous chlorides as a quantitative reducing agent will be found in Knecht and Hibbert's *New Reduction Methods in Volumetric Analysis* (see Appendix, p. 487). Titanous chloride, however, oxidises rapidly in air, and standard solutions of this salt must be kept in an atmosphere of hydrogen, and titrations should be carried out in an atmosphere of inert gas. Instead of attempting to preserve a standard titanous solution, it is better to make up a solution of a titanium salt of arbitrary strength, and reduce a measured volume of this as required. Titanous sulphate has advantages over the chloride, in that it is less easily oxidised by air, and back-titra-

tions can be carried out by means of potassium permanganate without difficulty.

" Titanous " sulphate is sold in the form of a solution which is rather less than normal. It contains titanic sulphate and must always be reduced before use. Thirty millilitres of this solution are diluted with 4N sulphuric acid to 250 ml. in a standard flask. This will give an approximately decinormal solution.

Standardisation of Titanous Sulphate.—Measure out 25 ml. of the diluted " titanous " sulphate solution into a 150 ml. stoppered bottle containing 100 grams of zinc amalgam, and add 25 ml. of 4N sulphuric acid. Replace the stopper and shake vigorously for at least one minute, in which time the deep brown colour due to partial reduction will have changed to violet. Pour off the aqueous liquid through a No. 3 sintered glass crucible into a filter-flask containing about 2 grams of sodium bicarbonate, and wash the amalgam twice with 4N sulphuric acid as described under the reduction of ferric alum (p. 126). To the titanous sulphate solution is added 0·1 gram of potassium thiocyanate, and it is then titrated with decinormal ferric alum until the brownish-red tint produced is permanent. The solution is warmed to 50° towards the end of the titration, placing the flask in a basin of water. Alternatively, the thick-walled filter-flask may be replaced by an ordinary Pyrex flask fitted with a rubber stopper bored with two holes, gentle suction being used.

Titanous sulphate, if free from iron, may also be standardised by means of potassium permanganate, in which case, after reduction, the titration may be carried out in the cold.

Iron

Determine the percentage of iron in iron wire by weighing accurately 0·56 gram of the wire, and dissolving it in a mixture of 20 ml. of water and 5 ml. of concentrated sulphuric acid. Run in dilute potassium permanganate solution until the smallest possible excess is present, and make up to 100 ml. Pour this into a burette, and titrate against 25 ml. of titanous sulphate as described above.

Chlorate

Prepare an approximately decinormal solution of potassium chlorate by weighing out accurately about 0·205 gram, dissolving, and making up to 100 ml. Measure out 25 ml. into a flask, and add about an equal volume of 4N sulphuric acid. Reduce 50 ml. of decinormal "titanous" sulphate by zinc amalgam as described on p. 161, and pour this into the chlorate solution. Warm to 50°, add 0·1 gram potassium thiocyanate, and titrate with decinormal ferric alum. If the titanous sulphate has been standardised by potassium permanganate, this reagent should be used to determine the excess, the small amount of chloride resulting from the decomposition of the chlorate being without effect on the permanganate.

Determination of Titanium in its Oxide or an Ore

Titanium may be determined by means of standard ferric alum, after solution and reduction of the sample. In the case of precipitated titanium oxide, solution can be effected by heating with concentrated sulphuric acid and ammonium sulphate, but in the case of ores such as rutile or ilmenite it is necessary to fuse with potassium pyrosulphate.

Determination of Titanium in Titanium Oxide—Weigh accurately about 0·7 gram of titanium oxide into a 250 ml. conical flask. Add 25 ml. of concentrated sulphuric acid and about 8 grams of ammonium sulphate. Heat with a small flame until the oxide has dissolved. After cooling, dilute with water and make up the solution to 250 ml. in a graduated flask. A trace of insoluble matter may be ignored, as it will probably be merely silica. Reduce 50 ml. of this solution by mercury amalgam, and titrate the titanous sulphate with decinormal ferric alum solution as described under the standardisation of titanous sulphate on p. 161.

Determination of Titanium and Iron in an Ore.—Grind the ore to a very fine powder in an agate mortar in small quantities at a time. Weigh accurately about 0·8 gram of the powder into a silica crucible, add about 6 grams of fused and coarsely powdered potassium pyrosulphate, and mix with a platinum wire. Fuse the mixture and extract the melt

as described on p. 387, but use only 50 ml. of water instead of 100 ml. Filter to remove any white residue which will consist of silica, wash with dilute sulphuric acid and make up the filtrate to 100 ml. in a graduated flask. Determine the titanium in 25 ml. of this solution with ferric alum as described above.

The iron content of the ore may be determined by reducing another 25 ml. of the solution with mercury amalgam and titrating with standard potassium permanganate. By deducting the volume of the latter, which is equivalent to the titanium only, from the volume used in the second titration, that equivalent to the iron is obtained.

STANDARD POTASSIUM BROMATE

(N/10 solution contains 2·784 grams of $KBrO_3$ per litre)

Potassium bromate in hot acidified solution reacts with certain reducing agents forming potassium bromide. When the reducing agents have been completely oxidised, any excess of bromate reacts with the bromide liberating free bromine, the presence of which may be detected by methyl orange or other azo dyes, which are at once decolorised.

Titration with standard potassium bromate solution may therefore be used to estimate antimony and arsenic (after these have been brought to the trivalent state), stannous chloride, and certain metals when in the form of their compounds with 8-hydroxy-quinoline (" oxines ") : also hydrazine and hydroxylamine.

Potassium bromate is easily obtained in a pure state, and is stable in solution. It is anhydrous, and should be dried at 120° before use.

Weigh accurately 2·784 grams of pure potassium bromate, dissolve in water and dilute the solution to 1 litre in a standard flask. If the potassium bromate is not pure (bromide is a common impurity), the solution must be standardised in one of the following ways :—

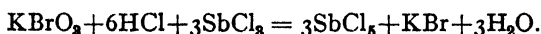
(1) Weigh accurately about 1·2 gram of pure arsenious oxide. Dissolve in 10 ml. of warm sodium hydroxide solution (p. 159), transfer the solution to a 250 ml. standard flask, add 5 ml. of concentrated hydrochloric acid, and dilute to the graduation mark. To 25 ml.

of the solution (measured from a burette) add 55 ml. of water and 20 ml. of concentrated hydrochloric acid. Titrate with the potassium bromate solution as described below under the determination of antimony.

(2) Weigh accurately about 0·15 gram of pure, finely divided antimony, and transfer to a 250 ml. conical flask. Add 20 ml. of concentrated hydrochloric acid and a few drops of bromine. Warm *very gently* until the antimony is dissolved, and then boil the solution until the excess of bromine is expelled. Reduce the antimonic to antimonious chloride and titrate with the potassium bromate solution as described below.

Antimony

When potassium bromate is added to a hot acid solution of antimonious chloride, the latter is oxidised to antimonic chloride:

$$KBrO_3 + 6HCl + 3SbCl_3 = 3SbCl_5 + KBr + 3H_2O.$$

If antimony is to be determined in presence of arsenic, the latter must be got rid of as indicated below. Tin, lead, silver, zinc, copper (less than 5 per cent.), and iron (less than 10 per cent.) do not interfere with the determination.

Procedure.—Place the weighed sample of the ore or alloy (corresponding to not more than 0·15 gram of antimony) in a 250 ml. conical flask, add 25 ml. of concentrated hydrochloric acid and about 0·5 ml. of bromine, and warm very gently until dissolved. Boil the solution to expel the excess of bromine.

Reduction of the Antimonic Chloride.—To the solution add 3 to 4 grams of sodium sulphite, rinse down the side of the flask with a little warm water, and boil the solution until the volume is reduced to rather less than 10 ml. Any arsenic that may be present is reduced and volatilised together with the excess of sulphur dioxide. If the sample is known to contain more than 2 per cent. of arsenic, add 20 ml. of concentrated hydrochloric acid and 5 ml. of sulphurous acid solution, and boil down again. Then add 20 ml. of concentrated hydrochloric acid and 70 ml. of water.

Titration with Potassium Bromate.—Heat the solution

until almost boiling. Run in the potassium bromate slowly (about 20 ml. per minute), with continuous brisk stirring, until most of the antimony is oxidised. Then add 2 ml. of methyl orange and continue the titration until the colour of the indicator disappears. The end-point is sharply defined.

If the methyl orange is added at the commencement of the titration, its colour gradually fades before the end-point is reached, and more indicator must then be added. A preliminary titration may be carried out in this way.

Exercise.—Determine the percentage of antimony in a sample of type metal (alloy of lead, antimony, and tin). Use about 0·5 gram of filings or thin foil.

Arsenic

Arsenic may be determined by means of standard potassium bromate in the same manner as described above for antimony.

Hydrazine

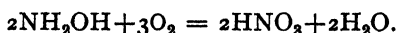
Hydrazine is oxidised by potassium bromate in a warm acid solution containing excess of potassium bromide. The resulting reaction may be represented by the equation $N_2H_4+O_2 = N_2+2H_2O$. So that 1 litre of decinormal potassium bromate is equivalent to $\frac{32{\cdot}05}{40}$ grams of hydrazine. An indicator such as indigo may be used to locate the end-point, or excess of potassium bromate may be added and the excess determined by means of potassium iodide and standard thiosulphate.

Prepare 100 ml. of an approximately decinormal solution of hydrazine by weighing accurately about $\frac{105}{400}$ grams of the hydrochloride, $N_2H_4,2HCl$, or about $\frac{130}{400}$ grams of the sulphate, N_2H_4,H_2SO_4, dissolving in water and diluting to 100 ml. in a graduated flask. Measure out 25 ml. of this solution into a flask, add 3 grams of potassium bromide dissolved in 20 ml. of water, and 20 ml. of concentrated hydrochloric acid. Heat to between 50° and 60°, and run in 0·1N potassium bromate (see p. 163) until the liquid shows a faint yellow colour, and

a drop removed by a glass rod gives a blue colour on potassium iodide-starch paper. The excess of bromate solution should be kept as small as possible to avoid loss of bromine. At once add 2 grams of potassium iodide, and quickly cool the solution to room temperature. Note the volume of bromate solution added, and titrate the liberated iodine with 0·1N thiosulphate. Deduct the volume of the bromate solution equivalent to the thiosulphate used from the volume of the bromate added, and calculate the hydrazine.

Hydroxylamine

Hydroxylamine is slowly oxidised by potassium bromate in acid solution to nitric acid and water in accordance with the equation :

$$2NH_2OH+3O_2 = 2HNO_3+2H_2O.$$

So that 1 litre of decinormal potassium bromate is equivalent to $\frac{33 \cdot 03}{60}$ grams of hydroxylamine. It is necessary to add excess of bromate and determine the excess by means of potassium iodide and standard thiosulphate.

Prepare 100 ml. of approximately decinormal hydroxylamine by weighing accurately about $\frac{69 \cdot 5}{600}$ grams of the hydrochloride, NH_2OH, HCl, dissolving in water and diluting to 100 ml. in a graduated flask. Measure out 25 ml. into a 200 ml. bottle, and add about 20 ml. of water. From a burette add 40 ml. of 0·1N potassium bromate. Fit a rubber cork carrying a small glass tap, and evacuate the air from the bottle. Then add 20 ml. of concentrated hydrochloric acid through a small funnel connected to the tap, but do not allow any air to enter the bottle. Remove and wash the funnel, mix the contents of the bottle, and allow to stand for twenty minutes. Add 2 grams of potassium iodide dissolved in 10 ml. of water through the funnel and tap. Mix the solution, let air into the bottle and titrate the liberated iodine with 0·1N thiosulphate. Deduct the volume of the bromate solution equivalent to the thiosulphate used, from the 40 ml. of bromate added, and calculate the hydroxylamine.

STANDARD POTASSIUM IODATE FOR USE IN PRESENCE OF 4N HYDROCHLORIC ACID

(*M/40 solution contains* 5·350 *grams* KIO_3 *per litre*)

The use of potassium iodate in solutions strongly acidified with hydrochloric acid was proposed by Andrews in 1903. It has been developed by Jamieson and others, and applied to the estimation of most reducing agents, and, indirectly, of oxidising and other substances.

The process depends on a series of reactions which take place consecutively in a solution about 4N with respect to hydrochloric acid. The potassium iodate is first reduced to potassium iodide, and this reacts with further potassium iodate to give free iodine. This is oxidised by still more potassium iodate to iodine *cations*, the ionised compound formed being iodine chloride.

Potassium iodate is easily obtained in a pure state, is stable in solution, and is unaffected by filter paper. The salt is anhydrous, and should be dried at 120° before use.

Make up 250 ml. of potassium iodate solution by dissolving 1·3376 grams of pure dry KIO_3 in water (M/40 grams per litre), and making up in a standard flask.

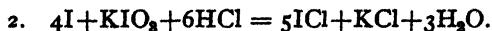
Iodides

If a solution of potassium iodate is added to one of potassium iodide containing *dilute* hydrochloric acid, the reaction takes place according to the following equation :—

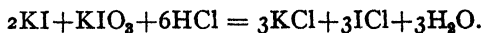
$$1.\quad KIO_3+5KI+6HCl = 6KCl+3H_2O+6I.$$

This reaction has been referred to in the standardisation of hydrochloric acid (see p. 75), and of sodium thiosulphate (see p. 140).

If the concentration of hydrochloric acid present is sufficiently high, the free iodine is oxidised by additional potassium iodate, iodine chloride being formed, and this is only stable in a strongly acid solution :—

$$2.\quad 4I+KIO_3+6HCl = 5ICl+KCl+3H_2O.$$

Combining these equations (multiplying (1) by 2, (2) by 3,

and adding) and simplifying, the final equation for the reaction becomes :—

$$2KI+KIO_3+6HCl = 3KCl+3ICl+3H_2O.$$

This reaction takes place in the presence of 12 per cent. or more of hydrochloric acid, but it is advisable to have the acidity of the solution not less than 4N at the end of a titration.

Procedure.—Make up a solution of potassium iodide by dissolving 1·66 grams in water, and diluting to 100 ml.

Measure out 10 ml. of the potassium iodide solution into a 250 ml. stoppered bottle, add 40 ml. of water, and 50 ml. of concentrated hydrochloric acid. Run in the iodate solution until the deep colour due to the iodine liberated at first has become pale brown. Now add about 5 ml. of carbon tetrachloride or chloroform, stopper the bottle, and shake vigorously. If the layer of organic solvent is strongly coloured, add about another millilitre of the iodate solution, and repeat the shaking. When the purple colour of the solvent has become pale, the iodate solution is added drop by drop, shaking after each addition, until the colour is completely discharged. The aqueous layer will remain yellow owing to the presence of iodine chloride. Should the end-point be overshot, a small measured volume of the iodide solution may be added, and the end-point redetermined.

From the equation deduced above, $KIO_3 \equiv 2KI$; so that

$$1 \text{ ml. of } M/40\ KIO_3 \equiv \frac{2\times 166\cdot 0}{40000} = 0\cdot 00830\ KI.$$

Copper

Copper is precipitated from a solution of its sulphate as cuprous thiocyanate, which is then titrated in presence of 4N hydrochloric acid with potassium iodate. The equation for the reaction is :—

$$2Cu_2[SCN]_2+7KIO_3+14HCl$$
$$= 7KCl+4HCN+4CuSO_4+5H_2O+7ICl.$$

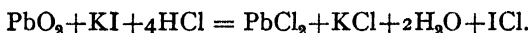
Procedure.—Weigh accurately about 0·35 gram of copper sulphate, dissolve in water, and make up to 100 ml. in a standard flask. Measure out 25 ml., and precipitate the copper as thiocyanate (see p. 301). Filter through a filter paper, and place the washed precipitate with the paper in a wide-mouthed

stoppered bottle. Add 50 ml. of water, and an equal volume of concentrated hydrochloric acid. Titrate with potassium iodate, finishing the titration as described under the estimation of iodides above.

Lead Dioxide

Lead dioxide and other oxidising agents can be determined by treating with excess of potassium iodide in the presence of 4N hydrochloric acid, and titrating the excess of potassium iodide with potassium iodate.

In the case of lead dioxide, the reaction is as follows :—

$$PbO_2+KI+4HCl = PbCl_2+KCl+2H_2O+ICl.$$

Procedure.—Weigh out accurately about 0·4 gram of lead dioxide, and wash this into a stoppered bottle. Add 25 ml. of decinormal potassium iodide, and a volume of concentrated hydrochloric acid about equal to the volume of liquid already in the bottle. Stopper and shake until the lead dioxide has dissolved. Now titrate with potassium iodate solution as described under the estimation of potassium iodide (p. 168). Knowing that PbO_2 is equivalent to KI (from the equation above), calculate from the excess of potassium iodide found, the percentage of lead dioxide in the sample taken.

Precipitation Processes

STANDARD SILVER NITRATE

(*N*/10 *solution contains* 16·99 *grams* $AgNO_3$ *per litre*)

STANDARD silver nitrate solution is used mainly for the determination of chloride, following either (1) Mohr's method of direct titration with potassium chromate as indicator, or (2) Fajans' method of direct titration with fluorescein or other adsorption indicator, or (3) Volhard's method in which the silver nitrate is used in conjunction with a standard solution of potassium (or ammonium) thiocyanate, with a ferric salt as indicator. The first and second methods are applicable only if the chloride solution is neutral. Volhard's titration is done in an acid solution and is of wider application. The same standard solutions of silver nitrate and potassium thiocyanate may also be used for the determination of bromide, iodide, and cyanide ; chlorate, bromate, and iodate ; silver and mercury.

A solution made by dissolving 16·99 grams of pure silver nitrate in water[1] and diluting to 1 litre is accurately decinormal. If ordinary commercial silver nitrate is used, an approximately decinormal solution is prepared (17 grams per litre) and is standardised with pure sodium chloride.

Standardisation of Silver Nitrate Solution.—If the silver nitrate is to be used in accordance with Volhard's method, it must be standardised by the method described on p. 177 ; if Mohr's or Fajans' method is to be followed, the solution is standardised as described below.

Dry the sodium chloride by heating it in a porcelain basin or fuse it in a platinum basin and break up the fused mass. Weigh accurately about 1·45 gram of the salt, dissolve it in water, and dilute the solution to 250 ml. in a standard flask. Titrate 25 ml. of the solution with the silver nitrate, as described in the next paragraph.

[1] It is essential that distilled water be used throughout all silver and halide determinations.

Titration of a Chloride Solution by Mohr's Method.—This method, in which potassium chromate is used as an indicator, is based on the fact that silver chromate is much more soluble than silver chloride (25 mgrms. as compared with 1·5 mgrm. per litre at 18°). If silver chromate, which is bright red, is shaken with sodium chloride solution, it is immediately converted into silver chloride; and if silver nitrate solution is added to a solution of sodium chloride containing a little potassium chromate, practically all the chloride will be precipitated as silver chloride before any silver chromate (recognised by its red colour) is permanently formed, and the end-point of the chloride precipitation is thereby indicated. The chloride solution must be neutral or very faintly alkaline, because silver chromate is readily soluble in dilute acid. If the solution is acid, it is usually permissible to neutralise it by adding a slight excess of pure calcium carbonate, which should be used instead of sodium carbonate or hydroxide, as these usually contain chloride.

Dilute 25 ml. of the chloride solution to about 70 ml. in a porcelain basin, and add 1 ml. of a 2 per cent. solution of neutral potassium chromate [1] (free from chloride). Run the silver nitrate slowly into the chloride solution, with constant stirring. Silver chloride is precipitated, and a red precipitate of silver chromate also forms locally, but disappears on stirring. After all the chloride is precipitated, however, the addition of more silver nitrate produces a permanent precipitate of silver chromate. Continue the titration, therefore, until a *faint* reddish-brown tinge persists even after brisk stirring. Until some experience has been gained, it is a common mistake to add too much silver nitrate. After completing the first titration, it is advisable, therefore, to destroy the reddish-brown coloration by adding a few drops of ammonium chloride and to keep the mixture (protected from daylight until required) as a guide for a second titration made in another similar basin. The first tinge of a permanent reddish-brown coloration is more easily observed by comparison with this mixture.

Before the permanent colour change that marks the end-point of this titration can be recognised, a certain minimum

[1] The side-shelf reagent (0·2N) is suitable. If the solution contains chloride, add a few drops of silver nitrate, and filter. Make a 1 ml. pipette (Fig. 28, p. 69) for measuring the potassium chromate solution.

amount of silver chromate must be permanently formed, and a measurable excess of silver nitrate is required to precipitate this minimum amount. The excess that is necessary depends on several factors, *e.g.* the solubility of silver chromate in the solution at the end-point, and the ability of the analyst to recognise slight colour changes. It is desirable to eliminate the personal factor as far as possible by making all determinations under the same conditions, *e.g.* amount of indicator, and volume of solution at the end-point. The unavoidable error amounts to, in general, at least 1 drop (about 0·05 ml.) of silver nitrate, *i.e.* at least 0·2 per cent. if the titration requires about 25 ml. of silver nitrate. No correction need be made, however, when standardising the silver nitrate solution if it can be arranged that approximately the same volume of silver nitrate (25 ml.) will be required when determining the amount of chloride in a solution, since in that case the titration errors will balance out.

Titration of a Chloride in Neutral Solution by Fajans' Method.—In this method the sodium salt of fluorescein plays the part of an indicator, but in a manner essentially different from that of potassium chromate in Mohr's process. If freshly precipitated silver chloride, after having been carefully washed, is suspended in a solution of sodium fluoresceinate, it retains its white appearance. If, now, a drop of silver nitrate solution is added to the suspension, the silver chloride at once becomes red in colour. The explanation of the colour change is as follows :—The fine particles of silver chloride readily adsorb either halide ions (already present) or silver ions (added as silver nitrate) whichever are in excess. In the former case they become negatively charged and in the latter positively charged. When, therefore, excess of silver nitrate is present, the particles can then adsorb the negatively charged fluorescein anions ; this causes the particles to change colour on account of the formation of red silver fluoresceinate on their surface. It must be carefully observed that the adsorption of the fluorescein ion by silver chloride and the resulting colour change occur only when an excess of silver ion is present in the solution surrounding the silver chloride.

If, therefore, silver nitrate solution is slowly added to a solution of sodium chloride containing fluorescein, no colour change is observed until the precipitation of the chloride is

complete and a minute excess of silver nitrate has been introduced. At this point, the suspended silver chloride becomes pale pink, and the colour change marks the end-point of a titration by Fajans' method. Substances like fluorescein, the action of which as indicators depends on the phenomenon of adsorption, have been described as "adsorption indicators." The indicator used for the titration of a chloride by this method is a 0·03 per cent. solution of the sodium salt of fluorescein,[1] and 1 ml. of the solution is taken for every 25 ml. of silver nitrate required. The chloride solution must be neutral or very faintly alkaline.

It must be noted that the colour change occurs, not in the solution, but on the surface of the silver chloride particles. It is more easily seen while the mixture is being stirred. The end-point is sharply defined and the titration error is almost negligible—not more than 0·1 per cent. (Compare Mohr's method.) A sharper end-point is obtained if the titration is completed somewhat rapidly, so that part, at least, of the silver chloride remains colloidal at the end-point. If the precipitate is completely coagulated, the adsorbing surface is much reduced and the colour change is evident only on the surface of the flocculated precipitate and is not apparent in the mixture as a whole.

Measure 25 ml. of the standard sodium chloride solution into a porcelain basin, add an equal volume of water and 1 ml. of the indicator solution. Run the silver nitrate slowly into the chloride solution, with constant stirring. (The precipitated silver chloride remains colloidal at first but coagulates freely near—at about 1 ml. short of—the end-point.) Continue the titration, meanwhile stirring continuously but not violently, until a permanent pink colour is suddenly observed in the turbid mixture.

The end-point is more readily perceived if the coagulation of the silver chloride has been entirely prevented by the addition of a solution of starch.

Repeat the above titration, adding, instead of 25 ml. of water, 10 ml. of water and 15 ml. of a freshly prepared 1 per cent. solution of starch.

If the concentration of the chloride solution is less than 0·01N, a sharp end-point is not obtained when fluorescein is

[1] This salt is sold as "soluble fluorescein."

used, and Fajans' method with this indicator is therefore not applicable to very dilute solutions of chlorides.

ANALYSES INVOLVING THE USE OF STANDARD SILVER NITRATE

Chloride, Bromide, and Iodide

Mohr's Method.—The chlorides and bromides of sodium, potassium, magnesium, and calcium, in neutral solution, may be determined by titration with standard silver nitrate, using potassium chromate as indicator. The procedure is described on p. 171. In the case of barium chloride it is necessary (since barium chromate is insoluble) to precipitate the barium by adding sufficient potassium sulphate. The precipitated barium sulphate does not interfere with the titration.

For iodides the method is unsatisfactory and should be avoided.

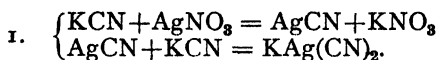
Fajans' Method.—The titration of the chlorides of sodium and potassium by this method, using fluorescein as an adsorption indicator, is described in the preceding section. In presence of divalent cations like calcium and magnesium, which cause immediate coagulation of the silver chloride precipitate, starch must be added to obtain an accurate result.

The bromides and iodides of sodium and potassium may be determined by the same method, the colour change at the end-point being very sharp, especially if the sodium salt of eosin is used. The titration of chlorides with this indicator is not possible, since silver chloride adsorbs eosin before the end-point is reached. A 0·05 per cent. solution of "soluble eosin" is prepared, and 1 ml. is used for every 25 ml. of decinormal silver nitrate required in the titration. Coagulation of the silver bromide occurs within 0·1 ml. of the end-point, and at the end-point the precipitate becomes brick-red. The colour change is much sharper than with fluorescein, and the titration error is negligible. With this indicator, bromide can be titrated in faintly acid solution (less than 0·1N acetic acid) with even greater precision than in neutral solution, and accurate results can be obtained with very dilute solutions (0·001N). Bromide cannot be titrated in presence of divalent cations with either fluorescein or eosin without the addition of one-third of the final volume of 1 per cent. starch solution (see p. 173).

Dichlorofluorescein (1 ml. of a 0·01 per cent. solution in 70 per cent. alcohol) may be used for the titration of chlorides, bromides, and iodides in neutral or weakly acid solutions, and may therefore be used in the titration of salts which undergo slight hydrolysis, such as the chlorides of copper and zinc. This indicator is more acidic in character than fluorescein, and its ions are more readily adsorbed by the silver halides. It is therefore much more suitable than fluorescein for the titration of a very dilute solution of halides.

Cyanide

When silver nitrate is added to a solution of an alkali cyanide, it produces, locally, a precipitate of silver cyanide which, however, dissolves in the excess of the alkali cyanide and forms a soluble complex cyanide :

$$1.\quad \begin{cases} KCN + AgNO_3 = AgCN + KNO_3 \\ AgCN + KCN = KAg(CN)_2. \end{cases}$$

After all the cyanide has been converted into this complex salt, the addition of more silver nitrate produces a permanent precipitate of silver cyanide :

$$2.\quad KAg(CN)_2 + AgNO_3 = 2AgCN + KNO_3.$$

The cyanide in a solution may therefore be determined by titration with standard silver nitrate until a *permanent* precipitate is produced. This indicates that all the cyanide has been converted into the complex salt, and marks the beginning of reaction 2. The addition of a few drops of potassium iodide makes the end-point sharper. In presence of ammonium salts, silver cyanide is not precipitated, and potassium iodide *must* be added as an indicator.

Procedure.—Add excess of sodium hydroxide and a few drops of potassium iodide to the cyanide solution contained in a beaker, and dilute the mixture until the concentration of the cyanide solution is less than 0·02 normal. Place the beaker on a sheet of *black* paper, and run the standard silver nitrate slowly into the cyanide solution, with constant stirring, until the first permanent opalescence appears.

One molecule of silver nitrate corresponds to *two* molecules of potassium cyanide, *i.e.* 1 ml. of normal silver nitrate corresponds to 0·1302 gram of potassium cyanide.

Exercise.—Determine the percentage of potassium cyanide in a sample of commercial cyanide. Weigh accurately 3 to 3·5 grams, dissolve in water together with about 2 grams of sodium hydroxide, and make up to 250 ml. in a standard flask. Measure *with a burette* 25 ml. of the solution for each titration, adding a few drops of potassium iodide solution. The commercial practice is to express the result as so much per cent. of *potassium* cyanide. As commercial cyanide is often mainly *sodium* cyanide, many samples give a "percentage" considerably above 100.

STANDARD SILVER NITRATE AND STANDARD POTASSIUM THIOCYANATE

When potassium thiocyanate is added to silver nitrate, a white precipitate of silver thiocyanate is produced. In order to mark the end-point, a ferric salt (free from chloride) is added to the silver solution. No ferric thiocyanate is permanently formed until all the silver is precipitated as thiocyanate, and the appearance of a permanent brownish coloration (ferric thiocyanate) shows when precipitation is complete. The titration must be performed in acid solution, and nitric acid is therefore added to the silver solution.

The thiocyanates of the alkalis are deliquescent salts, and a standard solution cannot be prepared by weighing a definite quantity. An approximately decinormal solution is therefore made by dissolving about 10 grams of potassium thiocyanate (or 8 grams of ammonium thiocyanate) in a litre. A solution of silver nitrate (approximately decinormal) is also required, and is made by dissolving 17 grams in 1 litre of water (see p. 170). These solutions are standardised as described below.

Preparation of the Indicator Solution.—Dissolve 5 grams of iron alum in 50 ml. of water, add 50 ml. of concentrated nitric acid (free from chloride), and boil the solution vigorously to expel oxides of nitrogen. Use 5 ml. of the solution for each titration.

Titration of Silver Nitrate with Potassium Thiocyanate.—The thiocyanate solution must be run into the silver nitrate solution, not *vice versa.* Add 5 ml. of the indicator solution to 25 ml. of the silver nitrate contained in a porcelain basin

dilute to about 75 ml., and then run in the thiocyanate slowly, with constant stirring. The first tinge of a permanent brown coloration marks the end-point. The brown coloration, which must persist after *brisk* stirring, is more easily seen if the precipitate is allowed to settle. After completing the first titration, destroy the brown coloration by adding about 1 ml. of silver nitrate, and keep this mixture as a guide for a second titration made in another similar basin (*cf.* p. 171).

After the silver nitrate solution has been standardised (as described in the next paragraph), the normality of the thiocyanate solution may be calculated.

Standardisation of the Silver Nitrate (*Volhard's Method*).—Weigh accurately 0·13 to 0·14 gram of pure, dry sodium chloride, and dissolve in 20 to 30 ml. of water in a small stoppered bottle. Add about 1 ml. of dilute nitric acid and 25 ml. of the silver nitrate solution. Shake the bottle vigorously until the precipitate coagulates and leaves the supernatant liquid clear. Filter[1] through a small paper into a porcelain basin. Rinse the bottle and wash the precipitate with cold water until all the silver nitrate is removed.[2] To the filtrate and washings add the ferric indicator, and titrate with thiocyanate.

Calculation.—It was found that 24·1 ml. of a thiocyanate solution was required for 25 ml. of a silver nitrate solution.

Of this silver nitrate, 25 ml. was added to 0·1320 gram of sodium chloride, and the filtrate required 1·21 ml. of the thiocyanate.

The excess of silver nitrate corresponds to 1·21 ml. of the thiocyanate $= 1{\cdot}21 \times \frac{25{\cdot}0}{24{\cdot}1} = 1{\cdot}25$ ml. of the silver nitrate solution.

[1] If the silver chloride is not removed by filtration, the end-point of the subseqent titration is indefinite and inaccurate, because silver chloride interacts with ferric thiocyanate and is converted into the *less soluble* silver thiocyanate. Pure potassium bromide (0·27 to 0·28 gram) may be used instead of sodium chloride for the standardisation and has the advantage that filtration is unnecessary, because silver bromide is less soluble than silver thiocyanate.

[2] To avoid washing the precipitate free from silver nitrate, the precipitation may be carried out in a standard flask, and an aliquot portion of the liquid taken for titration, after filtering through a dry filter and rejecting the first 10 ml. or so of the filtrate.

The volume of the silver nitrate solution corresponding to 0·1320 gram of sodium chloride is, therefore, 25 — 1·25 = 23·75 ml.

The silver nitrate is, therefore, $\frac{1000 \times 0 \cdot 1320}{23 \cdot 75 \times 58 \cdot 46}$ normal,
$= 0 \cdot 0951 N.$

Instead of separating the silver chloride from the liquid, its interaction with ferric thiocyanate (referred to in the footnote on p. 177) may be almost entirely prevented by the addition of 1 ml. of nitrobenzene for each 0·05 gram of chloride ion present before the addition of standard silver nitrate. The tightly stoppered bottle is then shaken for one minute, after which it will be found that the silver chloride has coagulated and carried down most of the nitrobenzene in such a manner that it not only protects the silver chloride from the action of the ferric thiocyanate, but also inhibits its darkening in the light. After addition of the ferric indicator, the excess of silver nitrate is slowly titrated with thiocyanate while the contents of the bottle are constantly swirled. The addition of the thiocyanate must be continued until the red colour persists for several minutes.

ANALYSES INVOLVING THE USE OF STANDARD SILVER NITRATE AND STANDARD THIOCYANATE

Chloride, Bromide, and Iodide

Chloride.—The determination of a chloride is carried out in a manner exactly similar to the method of standardisation described above.

To the chloride solution, acidified with nitric acid, add a measured volume of standard silver nitrate in *slight* excess, and shake or stir the mixture vigorously until the silver chloride coagulates and settles. Filter the silver chloride, and wash it with cold water. (If care has been taken to use quite a *small* excess of silver nitrate, very little washing is required.) Titrate the excess of silver nitrate in the filtrate with thiocyanate.

Exercise.—Determine the concentration of the dilute hydrochloric acid on the bench. Dilute 10 ml. to 250 ml. in a standard flask, and titrate portions of 25 ml. as described above.

Bromide.—In this case it is unnecessary to filter off the silver bromide before titrating the excess of silver nitrate, since the interaction of silver bromide with ferric thiocyanate is negligible. Otherwise the procedure is the same as for chloride.

Iodide.—When silver nitrate is added to an iodide solution, the precipitated silver iodide encloses a considerable amount of the soluble iodide or of the silver nitrate, and an error in the titration results. This may be lessened by dilution and shaking. The procedure must therefore be modified as follows :—

To a measured volume of the iodide solution, contained in a stoppered bottle, add a little nitric acid, and dilute to about 250 ml. Add standard silver nitrate gradually from a burette, 1 to 2 ml. at a time, and after each addition insert the stopper and shake the bottle vigorously. Continue the addition of silver nitrate until a slight excess is present, when the precipitate coagulates and the supernatant liquid becomes clear. Then add 5 ml. of the ferric indicator, and, without filtering, titrate the excess of silver nitrate with standard thiocyanate.

Chlorate

The chlorate is reduced to chloride by gently boiling with a considerable excess of sulphurous acid solution, or by saturating the cold solution with sulphur dioxide and then boiling for about five minutes. The excess of sulphur dioxide is then expelled by passing a current of carbon dioxide through the boiling solution for about twenty minutes, and the chloride in the solution is determined in the usual manner with standard silver nitrate and thiocyanate.

If there is any chloride in the chlorate, a separate portion of the solution must be titrated without previous reduction, and the amount of chloride so found must be deducted from the titre representing the chlorate plus chloride.

Exercise.—Determine the percentage of potassium chlorate in a sample of the commercial salt. Weigh accurately about 2·8 grams, dissolve in water, and dilute to 250 ml. in a standard flask. Use 25 ml. for each titration.

Silver

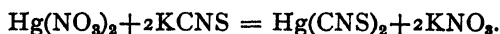
Silver may be determined by titration of a solution with standard thiocyanate in the usual manner. With the exception

of mercury, the presence of other metals does not, as a rule, interfere with the titration.

Exercise.—Determine the percentage of silver in a coin. Clean a silver threepenny piece with emery cloth and weigh it accurately. Place it in a 200 ml. conical flask, add 5 ml. of water and 10 ml. of concentrated nitric acid, and warm gently until the coin is dissolved. Add a little water, and boil for five minutes in order to expel oxides of nitrogen. Dilute the cold solution to 100 ml. in a standard flask, and use 25 ml. for each titration.

Mercury

Mercury can be determined in the same manner as silver by titration with standard thiocyanate. The solution must contain a considerable excess of nitric acid, and the mercury must be present as mercuric nitrate. The reaction which occurs during the titration is as follows :—

$$Hg(NO_3)_2+2KCNS = Hg(CNS)_2+2KNO_3.$$

As mercuric thiocyanate is somewhat soluble in water, it may not be precipitated ; but as it does not ionise appreciably this does not interfere with the titration, and no ferric thiocyanate is permanently formed until the above reaction is completed.

Procedure.—Weigh out accurately into a 300 ml. flask about 0·25 gram of mercury in the form of metal, oxide, or nitrate, and dissolve it in hot concentrated nitric acid diluted with an equal volume of water. Boil for a short time, cool, and make the solution faintly pink by the addition of decinormal potassium permanganate solution. Just discharge the pink colour by the cautious addition of very dilute ferrous sulphate. Add 5 ml. of concentrated nitric acid, 5 ml. of ferric alum indicator, and titrate with standard thiocyanate until a faint permanent brownish tint is obtained.

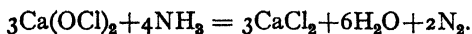
Exercise.—Determine by the above method the percentage of mercury in mercuric oxide.

Total Chlorine in Bleaching-Powder

Besides "available" chlorine, bleaching-powder may contain chlorine as chloride and chlorate which is useless for bleaching purposes (see p. 151). In order to determine

the total chlorine, prepare a solution of the bleaching-powder in the manner described on p. 151, and proceed as follows :—

Hypochlorite and Chloride.—Measure 25 ml. of the solution into a beaker, add 10 ml. of dilute ammonia, cover the beaker, and boil gently for about five minutes. The hypochlorite is thus converted into chloride, and nitrogen is liberated :

$$3Ca(OCl)_2+4NH_3 = 3CaCl_2+6H_2O+2N_2.$$

Add excess of dilute nitric acid, carefully avoiding loss through effervescence, and boil until free from carbon dioxide. Add excess of decinormal silver nitrate (25 to 30 ml.), stir until the precipitate coagulates, filter, and wash. Titrate the excess of silver nitrate in the filtrate with standard thiocyanate in the usual way.

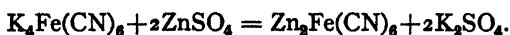
Hypochlorite, Chloride, and Chlorate.—Boil 25 ml. of the solution with dilute ammonia as before. Cool the solution and saturate with sulphur dioxide in order to reduce any chlorate to chloride. Boil for five minutes. Acidify with dilute sulphuric acid and expel the excess of sulphur dioxide by passing carbon dioxide through the boiling solution. (The last trace of sulphur dioxide may be destroyed by carefully adding dilute potassium permanganate until the solution is faintly pink.) All the chlorine in the bleaching-powder is now present in the solution as chloride, which may be determined by means of standard silver nitrate and thiocyanate in the usual manner.

The percentage of total chlorine in the bleaching-powder may then be calculated, and also (by difference) the percentage of chlorine present as chlorate. If the available chlorine in the same sample has been determined (pp. 151 and 159), the amount of chlorine which is present as chloride may also be calculated.

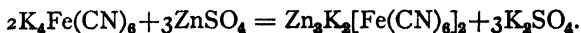
STANDARD POTASSIUM FERROCYANIDE

Zinc

When potassium ferrocyanide is added to an acid solution of a zinc salt, zinc ferrocyanide is first precipitated :

$$K_4Fe(CN)_6+2ZnSO_4 = Zn_2Fe(CN)_6+2K_2SO_4.$$

The addition of more potassium ferrocyanide converts the zinc ferrocyanide into the zinc potassium salt, and the complete

reaction may be represented by the following equation :—

$$2K_4Fe(CN)_6+3ZnSO_4 = Zn_3K_2[Fe(CN)_6]_2+3K_2SO_4.$$

The completion of the reaction may be determined by means of an external indicator—a solution of uranium nitrate. The use of an external indicator may be avoided by the method described by Cone and Cady (*J. Amer. C. S.*, 1927, vol. 49, p. 356), in which diphenylamine is added to the acidified zinc solution. This indicator, in the presence of ferricyanide accompanied by a zinc salt in solution, forms blue oxidation products, which are reduced by the least excess of ferrocyanide after all the zinc has been precipitated. Enough ferricyanide is usually present in ferrocyanide which has not been freshly prepared, but it is advisable to add a small amount if a new solution of ferrocyanide is being made up. As the ferrocyanide is run into the zinc solution, a blue colour is produced which at the end-point changes to a permanent greenish-yellow. If the end-point is accidentally passed, a standard solution of zinc sulphate may be used for back-titration.

It will be seen from the equation that the formula weight of potassium ferrocyanide is equivalent to 1·5 gram-atoms of zinc, so that a normal solution of ferrocyanide for the purpose of this reaction contains one-third of a gram-molecule of this salt in a litre.

The standardisation of the potassium ferrocyanide and the actual determination of the zinc should be carried out under as nearly as possible the same conditions. Oxidising and reducing substances, and other metals giving insoluble ferrocyanides, *e.g.* copper, cadmium, iron, cobalt and nickel, must be absent. Small amounts of lead and aluminium do not interfere.

The following solutions are required :—

Potassium Ferrocyanide.—Make up 250 ml. of approximately N/5 potassium ferrocyanide by dissolving 7·0 grams of $K_4Fe(CN)_6,3H_2O$, and 0·075 gram of potassium ferricyanide, in water and making up to 250 ml. in a standard flask. One ml. of this corresponds to about 0·0065 gram of zinc.

Standard Zinc Sulphate.—Make up 250 ml. of N/5 zinc sulphate by weighing out 7·189 grams of $ZnSO_4,7H_2O$, dissolving in water and making up to 250 ml. in a standard flask.

Indicator.—Dissolve 0·1 gram of diphenylamine in 10 ml. of concentrated sulphuric acid.

Standardisation of Potassium Ferrocyanide Solution.—Measure out 25 ml. of the zinc sulphate solution, add 20 ml. of 4N sulphuric acid, 5 to 10 grams of ammonium sulphate, and 50 ml. of water. Add not more than 3 drops of the diphenylamine solution, and titrate with the ferrocyanide in the cold. The greenish-yellow colour when first obtained reverts to blue on standing, and ferrocyanide must be added drop by drop until it is permanent.

Exercise.—Determine the percentage of zinc in a sample of commercial zinc oxide (zinc white). Weigh accurately about 2 grams of the oxide. Dissolve in 25 ml. of 4N sulphuric acid, dilute the solution to 250 ml. in a standard flask, and titrate 25 ml. containing the same amounts of ammonium sulphate and sulphuric acid as indicated above.

This method can be applied to the determination of zinc in ores, after precipitating the zinc as sulphide. This is dissolved in 10 ml. of concentrated hydrochloric acid and 90 ml. of hot water. The hydrogen sulphide liberated must be expelled by boiling, after which the solution is just neutralised by ammonia. The procedure as given under the standardisation of potassium ferrocyanide is then followed.

STANDARD POTASSIUM IODATE

Barium

The barium salt solution is treated with a measured excess of standard potassium iodate. The solution and precipitated barium iodate are transferred to a standard flask, made up to the mark, and the excess of potassium iodate determined in an aliquot part by adding excess of potassium iodide, acidifying, and titrating with standard sodium thiosulphate.

Prepare a standard solution of potassium iodate by weighing accurately about 3·2 grams of pure potassium iodate, dissolving this in about 75 ml. of water, and making the solution up to the mark in a 100 ml. standard flask.

Determine the percentage of barium in crystalline barium chloride by weighing accurately about 0·2 gram of the salt and dissolving it in 20 ml. of water in a 100 ml. beaker. Support a dropping-tube (p. 236) so that the drawn out tip touches the side of the beaker well above the surface of the

liquid and heat the solution to the boiling-point. Keep the liquid gently boiling and with a pipette run 25 ml. of the standard potassium iodate through the dropping-tube while stirring the liquid in the beaker. When the pipette has drained for fifteen seconds, remove it and wash the dropping-tube several times with small quantities of water. Boil the liquid gently for a minute while stirring and allow it to cool to room temperature. Transfer the liquid and precipitate to a 100 ml. standard flask, carefully washing the beaker, stirring rod, and funnel with small quantities of water. Make up to the mark with water and mix. After one hour filter the solution through a small dry filter, neglecting the first few millilitres which pass through the filter.

Titrate an aliquot part of the filtrate as follows :—Dissolve 2 grams of potassium iodide in 25 ml. of water, add about 0·5 gram of sodium bicarbonate, and 10 ml. of dilute sulphuric acid. Run in 10 ml. of the filtrate with a pipette, and titrate the liberated iodine by means of approximately N/10 sodium thiosulphate. Repeat the titration on another 10 ml. of the filtrate. Now standardise the sodium thiosulphate solution by taking another 25 ml. of the original potassium iodate solution and diluting it to 100 ml. in the standard flask used above. Mix, and titrate 10 ml. of the diluted solution exactly as described in the determination of the excess of potassium iodate in the filtrate from the barium iodate.

If W = the weight of KIO_3 in 25 ml. of the standard solution,

V_1 = the volume of $Na_2S_2O_3$ required to titrate 10 ml. of the filtrate,

and V_2 = the volume of $Na_2S_2O_3$ required to titrate 10 ml. of the diluted standard KIO_3,

then 1 ml. of $Na_2S_2O_3$ is equivalent to $\frac{W}{10V_2}$ grams of KIO_3.

The weight of KIO_3 used in precipitating barium is equivalent to $(10V_2-10V_1)$ ml. of $Na_2S_2O_3$ and is therefore

$$W\left(1-\frac{10V_1}{10V_2}\right) \text{ grams.}$$

Thus the weight of Ba precipitated $= \frac{137{\cdot}4W}{2\times214}\left(1-\frac{10V_1}{10V_2}\right)$.

STANDARD BARIUM CHLORIDE

Sulphate

Sulphates in acid or neutral solution can be determined by means of standard barium chloride, using a solution of sodium rhodizonate as indicator. This indicator gives a red coloration with a solution of a barium salt, whilst if a solution of a sulphate is added in excess the solution is yellow if neutral or nearly colourless if acid. The indicator may either be added to a measured volume of the standard barium solution, or it may be applied to a filter paper and drops of the solution being titrated tested by placing them on the treated paper. If the first method is used it is essential to run the sulphate into the barium solution containing the indicator, and this procedure is preferable if the indicator is used externally. If sulphite is present, excess of formaldehyde must first be added.

Prepare a solution of the indicator by dissolving 0·02 gram of sodium rhodizonate in 10 ml. of water. This must be freshly made up as the solution does not keep. Filter paper moistened with the reagent and stored in an evacuated desiccator over calcium chloride will remain effective for a few days.

Exercise.—Prepare 250 ml. of decinormal barium chloride solution and 100 ml. of a decinormal solution of sodium sulphate. Measure out 25 ml. of the barium chloride solution, add 5 to 8 drops of the indicator and run in the sulphate solution from a burette until the red colour changes to yellow. Now repeat the titration without adding the indicator, and when an amount of the sulphate solution has been added within 0·5 ml. of that previously required place a drop of the liquid on a filter paper moistened with the indicator solution. A red stain should be produced by the barium still in solution, but on continuing the titration a point will be reached when a drop no longer gives a red stain.

Determine the concentration of an approximately decinormal solution of sulphuric acid as described above. In this case the yellow colour is discharged in the spotting test when all the barium has been precipitated.

STANDARD THORIUM NITRATE

Fluoride

Fluorides may be determined by a method depending on the fact that thorium fluoride is precipitated when thorium nitrate is run into a dilute solution of a fluoride at a suitable *p*H. The end-point is indicated by the formation of a pink colour when excess of thorium has been added to the fluoride solution containing sodium alizarin sulphonate.

The following solutions are required :—

(1) **Thorium Nitrate Solution.**—Prepare an approximately decinormal solution by dissolving 3·44 grams of thorium nitrate in water, and diluting to 250 ml.

(2) **Sodium Alizarin Sulphonate.**—Dissolve 0·05 gram of this indicator in 100 ml. of water.

(3) **Buffer Solution.**—Dissolve 4·724 grams of monochloracetic acid in 25 ml. of N sodium hydroxide, and dilute to 50 ml.

(4) **Standard Ammonium Fluoride Solution.**—Dissolve 0·4868 gram of pure ammonium fluoride in water, and dilute to 250 ml. One ml. of this solution contains 1 mgrm. of fluorine.

Standardisation of Thorium Nitrate Solution.—Measure out 50 ml. of the ammonium fluoride solution into a conical flask, add 50 ml. of water, and 12 drops of the indicator solution. Make the mixture alkaline (pink) by adding a drop of normal sodium hydroxide, and then just discharge the pink colour by careful addition of decinormal hydrochloric acid. Add 1 ml. of the buffer solution to produce a *p*H of approximately 3, and run in the thorium solution while shaking until a faint permanent pink colour is visible. Fifty ml. of the fluoride solution should require 26·3 ml. of N/10 thorium nitrate solution. A blank experiment should be carried out on 100 ml. of water containing the same amounts of indicator and buffer solution as above.

Exercise.—Determine the percentage of fluorine in sodium or potassium fluoride, using a solution containing approximately 1 mgrm. of fluorine per ml.

Electrometric Methods

ACIDIMETRY

REFERENCE has already been made (p. 63) to the determination of the hydrion concentration of a liquid by means of electrical measurements, and to the detection in this way of the point of rapid change in pH which is found to occur whenever a stoichiometric point is reached in the titration of an acid by an alkali. Such methods, depending as they do on the observation of the movement of the needle of a galvanometer, are free from the personal factor involved in the matching of tints or the detection of changes in colour of a liquid, and are in addition applicable to cases in which the turbidity or original colour of the liquid makes the use of an indicator difficult. To determine the *absolute* value of the pH of a solution accurately by electrometric methods demands, however, meticulous care in the preparation of standards, and considerable technique in the carrying out of the experimental work, combined with expensive and possibly complicated apparatus, while unexpected sources of error are liable to affect the results. For the theory and accurate carrying out of such determinations, special works must be consulted. But the detection of a considerable change in pH is a much simpler matter, and the stoichiometric point of a titration can be determined with an accuracy equal to that of ordinary volumetric analysis by the use of simple apparatus and the exercise of ordinary care. Similarly, approximate determinations of pH can be made, possibly useful in themselves, and certainly serving as an introduction to more exact work. Such simplified methods only will be dealt with here.

The Half-Cell, and its Potential

The reader will be familiar with the constitution and working of the ordinary simple electric cell, in which two metals immersed in a common solution produce an electric

current when connected outside the cell. This current is due to a *difference* in potential between the two metals or " poles " which provides the electromotive force. Each of the poles possesses by itself a potential which results from the tendency that exists for ions of the metal to pass into the solution, a tendency that depends on the nature of the metal and of the solution with which it is in contact, and also on the concentration of the ions of the metal already present in the liquid. This potential is quite uninfluenced by the presence of the other pole, and will remain the same if the cell is divided into two parts, leaving no connection either internally or externally between the two metals. Such an arrangement, consisting of a single pole in a solution, is called a " half-cell." To obtain an electromotive force, this half-cell must be joined by a bridge or siphon of a conducting liquid to another half-cell containing either a different metal, or a different solution, or both. The E.M.F. generated by the combination may be determined by a calibrated potentiometer and galvanometer.

It will be seen from the above that the potential generated when a metal is immersed in a certain solution, though not capable of measurement by itself, may be determined when we combine the half-cell thus formed with another whose potential is already known, and then measure the E.M.F. generated by the pair ; while to follow the change in potential due to any alteration in the liquid of a half-cell, it is sufficient to combine it with any other half-cell whose potential remains constant during the period of the experiment.

To determine the actual pH of a solution, or to follow any change in its hydrion concentration due to the addition of a reagent, all that is required, therefore, is to use it as the liquid of a half-cell which has a pole capable of receiving or giving up hydrions ; and to combine this half-cell, by means of a non-interfering " bridge " of conducting liquid with another half-cell whose potential is either known or constant. The potential of a hydrogen pole in the presence of a normal concentration of hydrions is taken as the standard to which all other half-cell potentials are referred ; and hydrogen poles would seem to be desirable in the half-cells. The difficulty of handling hydrogen gas as a pole can be overcome by adsorbing the gas by means of finely divided platinum on a foundation of platinum wire or foil, the platinum black being

kept saturated with hydrogen by continuously bubbling the gas past it.

The hydrogen electrode formed in this way, however, though simple in theory, is rather troublesome in practice, and is very sensitive to adventitious influences, so that wherever possible some substitute is used. As a standard half-cell, a calomel electrode is almost universally employed, in which there is a pole of mercury in contact with a solution of potassium chloride saturated with calomel, the potential of such an arrangement under definite conditions being known accurately. Where, again, a solution is acid and free from oxidising and reducing substances and from ammonium salts, the addition to it of a little quinhydrone gives with a pole of clean platinum an almost perfect substitute for the hydrogen electrode. In the presence of oxidising agents the hydrogen electrode cannot be employed, and should theoretically be replaced by one of oxygen. Instead of this a pole consisting of a metal and its oxide—antimony has been found the most suitable—may be used.

TITRATION OF ACIDS

In the case of a titration it is not necessary to measure the *p*H absolutely, but only to decide the point of maximum change in *p*H for the addition of a definite small amount of reagent. The standard half-cell may therefore be replaced

Complete Cell

Half-cell with changing potential: *e.g.* platinum pole in acid liquid being titrated after addition of quinhydrone.	Bridge of conducting solution.	Half-cell with fixed potential: *e.g.* platinum pole in solution of a salt after addition of quinhydrone.[1]

[1] This salt solution is preferably buffered (see p. 270, footnote) to prevent changes in *p*H during the experiment due to carbon dioxide from the air or alkali from the glass.

by any half-cell which gives a constant value ; and the procedure consists in investigating by means of a potentiometer, which need not be standardised, and a sensitive galvanometer, the potential difference generated by a cell built up as shown in the above table.

The following apparatus is required :—

Platinum Poles.—To make a platinum pole a piece of narrow soft glass tubing about 15 cm. in length is drawn out to a capillary, and this is cut off short. A platinum wire about 1 cm. long is pushed into the narrow opening so that half projects outside, and the glass is melted round the wire, the end being gently blown out so that the glass is of regular thickness. It is annealed by cooling slowly a few inches above the flame. Contact between the wire and the outside circuit is made by means of a little mercury poured into the tube into which a clean copper connecting wire can be dipped. Before use the platinum is cleaned by dipping into chromic acid mixture (p. 47), and then rinsing with distilled water. In use the wire only should be immersed in the liquid.

Quinhydrone, which in acid titrations must be added to the liquid, is a slightly soluble crystalline organic compound of a complex character, which in a solution of *p*H less than 8 gives with a platinum wire a potential which depends on the concentration of hydrions present. A little of the solid, sufficient to leave some undissolved, is stirred into the solution in which the platinum pole is inserted. The final potential is reached in about a minute.

Connecting Bridge.—It is necessary to connect the two solutions in the half-cells by a conducting liquid, and a difficulty is met with in the fact that a diffusion potential is always set up at the junction of solutions which differ either in composition or concentration. Since this potential depends on the speed of migration of the ions, it may be almost nullified by selecting as a connecting medium the solution of a salt of which the positive and negative ions have approximately the same speed. Potassium chloride solution is most commonly used.

The simplest form of bridge is a glass siphon with short arms. The potassium chloride solution, which is conveniently of normal strength, may be retained in the siphon by plugging the ends of the tube with cotton-wool. It is more convenient to use siphons filled with an agar jelly, which is made by heating about 1 gram of agar in 30 ml. of the potassium chloride solution on a steam-bath for about an hour, filling the siphons, and leaving to stand until set. Contraction may be allowed for by fitting short pieces of rubber tubing onto the ends of the siphon, and removing these with any excess jelly

afterwards. Such bridges may be used many times. They are washed with distilled water before and after use, and kept in the potassium chloride solution.

Electrical Instruments.—Results of a sufficient degree of accuracy may often be obtained by the use of a sensitive galvanometer alone, combined with a control resistance in series which can be cut out gradually. No actual readings of the swing of the needle can be taken, for the instrument must be used only to detect the point when no current flows from the combined

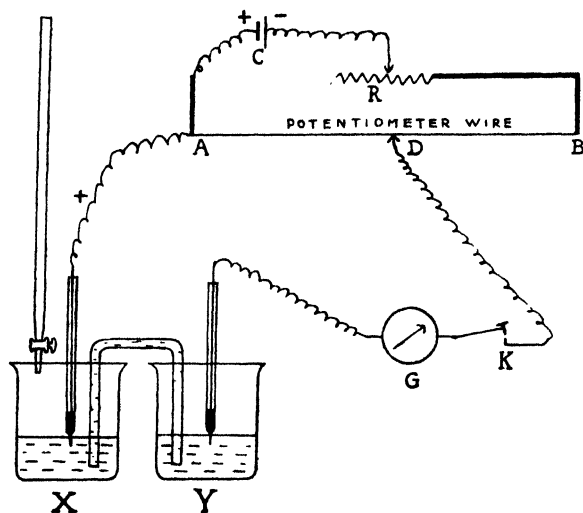



FIG. 36.

half-cells, one of which contains the solution being titrated, and the other a solution of the salt which is formed by the reaction being studied.

To follow the course of the titration it is necessary to use a potentiometer, the simplest form of which consists of a wire stretched over a metre rule (Fig. 36), the ends A and B being connected through a regulating resistance R, with the terminals of an accumulator or good dry cell C. In this way there is produced a regular fall of potential along the wire, and the difference of potential between any two points on the wire A and D will be proportional to the distance between them.

The pole of the half-cell X containing the acid which is being titrated is joined to the positive (and zero) end A of the

potentiometer wire by a direct connection, and the pole of the half-cell Y of fixed potential is connected through a sensitive galvanometer G to a contact D which can be moved along the wire. A position is found in which no current flows through the galvanometer when contact is made with the wire, and the length of wire AD intercepted is read. This process is repeated after each addition of the titrating alkaline solution, the connections with the half-cells being reversed when the zero is reached.

When the zero-point has been passed, the lengths recorded may then be graphed against the volume of alkali added up to each point, and the position of maximum slope of the curve found from the graph ; or the change in length may be divided in each case by the additional volume of alkali which produced it, and the point of maximum change per unit addition judged from the results.

Exercises (1)—**Electrometric Titration of Acid, using Galvanometer only.**—Prepare approximately decinormal solutions of sodium hydroxide and hydrochloric acid. Titrate 25 ml. of the acid with the sodium hydroxide, using methyl-orange as indicator.

Pipette 25 ml. of the hydrochloric acid above into a wide 100 ml. beaker, and into a similar beaker put a convenient volume of approximately twentieth-normal sodium chloride solution. Add a little quinhydrone to each, and stir. Immerse in each a platinum pole, and connect the two vessels with a potassium chloride-agar bridge. Connect up the apparatus through a box of resistance coils to a galvanometer, putting a key in the circuit. Arrange the burette containing the sodium hydroxide above, so that this can be run into the acid. Add the alkali at first in quantities of 5 ml., reducing the amount to 2 ml., and finally to single drops as the point of neutralisation previously obtained is approached. After each addition depress the galvanometer key cautiously. When no deflection can be observed in the " acid " direction, take the reading of the burette. Continue to add alkali in drops until a deflection is observed in the opposite or " alkali " direction. Take this reading. The difference between the two readings will show the sensitiveness of the arrangement, and the result should be compared with that obtained by the indicator method.

(2) **Electrometric Titration of Acid, using Potentiometer.**—Connect up the apparatus as shown in Fig. 36, placing 25 ml. of the hydrochloric acid in the vessel X, and some dilute acetic acid containing sodium acetate in Y. Proceed as in (1) above with the addition of the sodium hydroxide, but now move the contact on the potentiometer wire after each addition to such a position that there is no deflection observable in the galvanometer when contact is made. Record the potentiometer readings and the burette readings in parallel columns. The former may become negative in sign after the neutral point is passed, when the connecting wires to the platinum poles must be interchanged. Do not continue the addition of alkali more than 0·2 ml. beyond this point. Plot the results on squared paper, marking off the burette readings horizontally, and the potentiometer readings vertically, the latter being negative after an interchange of poles. Decide by means of a straight-edge the burette reading which corresponds to the steepest slope of the curve through the points recorded.

Calculate also the change in the potentiometer reading *per millilitre added* for each successive addition of alkali. Decide at what reading of the burette this change is greatest. Compare the results with those obtained with methyl orange, and by method (1).

Repeat the above series of experiments, using a decinormal solution of acetic acid instead of the hydrochloric acid. The indicator used for comparison must be phenolphthalein, and in method (1) it is probable that no deflection will be detectable until the point of neutralisation is passed.

By one of the above electrical methods, find the percentage of acetic acid, $CH_3.COOH$ (Eq. wt. = 60), in a sample of brown vinegar.

THE DETERMINATION OF *p*H

To find the *p*H of a solution, it must form the liquid of a half-cell with a hydrogen pole, and be connected by a conducting bridge with another half-cell of known potential. The E.M.F. of the combination is then measured by means of a standardised potentiometer, and the potential of the unknown half-cell deduced. From this the value of the *p*H of the liquid is obtained by the use of an established formula.

As has been already stated (p. 189), a calomel half-cell is usually employed as the half-cell of known potential. If the *p*H of the unknown solution is less than 8, a platinum pole and quinhydrone is used for this. If it is greater than 8, a pole of hydrogen gas must be used, in which case the known half-cell may also consist of a hydrogen gas pole in a liquid of known *p*H (Cole, *Practical Physiological Chemistry*).

The Calomel Half-Cell

This is most simply constructed by fitting a small wide-mouthed glass bottle with a rubber stopper bored with two holes, one of the correct width to take a platinum pole (p. 190), and the other wide enough for a glass tube through which one of the arms of a bridge will pass easily. The lower end of this wide tube should be just below the stopper and the upper end be widened so that it may be closed by a cork when the half-cell is not in use. The platinum pole is inserted through the stopper so that the end of the wire almost touches the bottom of the bottle. Pure mercury is poured in so that the platinum wire is well covered, even if the bottle is accidentally shaken. Some pure calomel and mercury are rubbed into a paste in a mortar with some of the potassium chloride solution to be used in the cell, and this is then poured onto the mercury. The bottle is then nearly filled with the potassium chloride solution, which should previously have been saturated with calomel. The bridge used to connect this half-cell with that under investigation should have been made with potassium chloride solution of the same strength.

The strength of the potassium chloride solution used in the calomel half-cell should be saturated, normal, or decinormal, and of these the normal solution is most convenient for ordinary use.

Calculation of *p*H for the Combination of Quinhydrone and Calomel Half-Cells

For the theory and deduction of the formulæ applying to half-cells, reference must be made to such a book as Grant's *Measurement of Hydrogen Ion Concentration*. When a calomel half-cell made up with normal potassium chloride is used in conjunction with a platinum pole and quinhydrone

in the liquid under investigation, the pH of this liquid is given by the following formula :—

$$pH = \frac{e_{quin} - E - e_{cal}}{0{\cdot}198T}$$

Where E is the E.M.F. observed in millivolts,
T is the absolute temperature,

e_{quin} is 704·4 mv. at 18°, rising with fall of temperature approximately 0·75 mv. per °C.

e_{cal} is 286·4 mv. at 18°, rising with fall of temperature approximately 0·2 mv. per °C.

The combined value of $e_{quin} - e_{cal}$ is 418 mv. at 18° C., rising 0·5 mv. for each fall of 1° C.

Exercise.—Prepare 100 ml. of 0·2N acetic acid and 100 ml. of a 0·2N solution of sodium acetate.

Set up the apparatus as in Fig. 36, and calibrate the potentiometer wire as follows :—In place of the half-cells, connect a standard cadmium cell between the positive end of the potentiometer wire and the galvanometer. Find the balancing point on the wire, and thence calculate the fall in potential in millivolts per centimetre of the wire, taking the E.M.F. of the cadmium cell to be 1018 mv.

The cadmium cell is now replaced by the two combined half-cells, X and Y, the latter being the calomel half-cell. Into a small wide beaker measure from a burette 32·8 ml. of the 0·2N acetic acid, and 7·2 ml. of the 0·2N sodium acetate solution. This will give a solution of pH value 4·0. Stir in a little quinhydrone, insert a platinum pole, and connect with the calomel half-cell by means of an agar bridge of normal potassium chloride. The acetate half-cell X is connected to the positive end of the potentiometer wire. After a minute or so, find the balancing point on the wire, and convert the reading into millivolts.

Calculate the pH of the acetate solution by means of the formula given above.

Repeat the experiment, using a mixture of 12 ml. of 0·2N acetic acid with 28 ml. of 0·2N sodium acetate in the half-cell X. The pH value of this solution is 5.

The Hydrogen Electrode

A simple hydrogen electrode may be made as follows :— A platinum wire mounted as described on p. 190 is carefully cleaned, first with fine emery paper, then by immersion for a short while in warm chromic acid mixture (p. 47), finally washing in distilled water. It is then coated all over with a thin coherent layer of platinum black, by making it the cathode in a cell with a platinum anode in a 3 per cent. solution of platinic chloride acidified with hydrochloric acid. As soon as the bright metal is completely hidden by the black deposit, the electrode is washed in distilled water, and the electrolysis continued in a 10 per cent. solution of sulphuric acid. Hydrogen should escape uniformly from the surface. If it does not do so, the wire must be again cleaned, and the process repeated. A prepared electrode must not be allowed to dry, and is stored in distilled water.

The half-cell containing the hydrogen electrode is arranged so that this is immersed in the liquid, and bathed in a continuous current of pure hydrogen, which bubbles past it rapidly until saturation has been attained, and then more slowly. If obtained from a cylinder of pure gas, it is sufficient to pass the hydrogen through a wash-bottle containing alkaline 2 per cent. potassium permanganate ; but if it is being generated from a Kipp, it should also be passed through a solution of mercuric chloride ; in either case, it is passed finally through a wash-bottle containing the same liquid as that surrounding the electrode.

Determinations of pH by means of the hydrogen electrode are carried out as described in the exercise on p. 195, and the pH is calculated from the formula :

$$pH = \frac{E - e_{cal}}{0{\cdot}198T}$$

E being the observed E.M.F. in millivolts, and T the absolute temperature. The value of e_{cal} is given on p. 195.

The Glass Electrode

Another form of electrode which offers certain advantages over those considered above is the glass electrode. Its use depends on the fact that a difference of potential exists between

a glass surface and a liquid with which it is in contact, the *p*H of the liquid determining the magnitude of this difference of potential. The apparatus consists of a thin glass diaphragm between two liquids, one of which is of known *p*H, and the other is the liquid under investigation. Its chief advantages lie in the facts that it is unaffected chemically by the solution whose *p*H is being determined, and that it can be used for a wide range of *p*H values. Its high resistance entails the use of more complicated apparatus than that already described. In conjunction with special thermionic valves, it is likely in the future to displace earlier forms of electrodes for industrial work.

REDUCTION-OXIDATION SYSTEMS

According to the modern view, all reduction-oxidation reactions involve a transfer of electrons, the system which is being reduced gaining electrons, and the system which is being oxidised losing electrons. Thus a change from the ferrous ion to the ferric ion involves the loss of one electron—$Fe^{\cdot\cdot} - e \rightleftharpoons Fe^{\cdot\cdot\cdot}$; while the change from the ferricyanide ion to the ferrocyanide ion involves the gain of one electron: $Fe(CN)_6''' + e \rightleftharpoons Fe(CN)_6''''$. In reactions in which iodine is concerned, the oxidation of an iodide ion to free iodine involves the loss of one electron from each iodide ion ; and the oxidation of free iodine to a positive iodine ion (as in titrations with potassium iodate in strongly acid solution), involves a further loss of one electron by each atom of iodine :

$$I' - e = I \quad \text{and} \quad I - e = I^{\cdot}.$$

When an unattackable electrode such as platinum is placed in an oxidising solution, the electrode tends to lose electrons and thereby acquires a positive potential with respect to the solution. This can be measured, and gives an indication of the oxidising tendency of the solution. Such a potential is called the " reduction-oxidation " potential of the solution, or, more briefly, the " redox " potential.

The redox potential, then, is the positive potential acquired by a platinum electrode immersed in the oxidising solution.

This potential only has a definite value where *both* the oxidised and reduced forms of the system are present in definite amounts. Further, the system must be reversible

thermodynamically, that is to say, the application of an infinitesimal potential from an external source must suffice to convert one form of the system into the other. In such a case the redox potential of the system, E, can be expressed by the equation :

$$E = E_o + f \log_e \frac{[\text{oxidised state}]}{[\text{reduced state}]}$$

in which the square brackets represent concentrations or activities, and f is a factor which is constant for the system at any particular temperature. Since the logarithm of unity is zero, it will be seen from this equation that when both oxidised and reduced states are present in equal concentrations, the observed potential is always the same for a given temperature for that system. This potential, represented by E_o in the equation, is called the standard redox potential of the system. The approximate value of E_0 in some of the systems made use of in oxidation and reduction processes are given in the table.

Standard Reduction-Oxidation Potentials.

	Volts
Acid permanganate—manganous	1·52
Ceric—cerous (in H_2SO_4 solution)	1·44
Dichromate—chromic	1·3
Ferric—ferrous	0·75
Acid arsenate—arsenite	0·57
Iodine—iodide	0·4
Alkaline arsenate—arsenite	0·15
Titanic—titanous	0·06
Stannic—stannous	—0·15

Any system in the table will oxidise one lower in the list, the completeness of the oxidation depending on the difference between the values of E_0 for the two systems. Thus in acid solution an arsenate oxidises potassium iodide liberating iodine ; while in a solution made slightly alkaline with sodium bicarbonate the converse reaction takes place, free iodine converting an arsenite almost completely to arsenate.

Reduction-Oxidation Titration by Electrometric Methods

When a system in the reduced state is gradually oxidised its potential will rise, and it will be seen from the equation given above that this rise will not be regular. As a ratio

approaches unity its logarithm changes more slowly, so that if we start with a completely reduced system and gradually oxidise it, the potential at first rises rapidly, and then more slowly. After the mid-point of the conversion the potential again rises slowly at first, and then more rapidly, so that a curve, the centre part of which is flattened, could be drawn. From such a curve, however, the mid-point of the conversion of the reduced system could not be determined accurately.

The approximate position of the end-point of the titration, when the potential has risen to that of the completely oxidised system, can be found by balancing a half-cell containing the liquid which is being titrated against one containing the fully oxidised system, and this method is used in the following exercises.

Exercise (1)—**The Titration of a Ferrous Salt with Potassium Dichromate.**—Prepare approximately decinormal solutions of potassium dichromate and ferrous ammonium sulphate as described on pp. 118 and 120. Titrate 25 ml. of the ferrous solution with the dichromate, using potassium ferricyanide as an external indicator.

Carry out the electrometric titration of further portions of 25 ml. of the ferrous ammonium sulphate in a manner similar to that described on p. 192 (Exercise 1), adding dilute sulphuric acid to the ferrous solution, but no quinhydrone. The fixed-potential half-cell should contain a solution of ferric alum acidified with dilute sulphuric acid. The end-point is reached when no movement can be detected in the galvanometer. Compare the result obtained with that given by the titration in which potassium ferricyanide was used as an external indicator.

Exercise (2)—**The Titration of Potassium Ferrocyanide with Potassium Permanganate.**—Carry out a similar experiment to that above, titrating an approximately decinormal solution of potassium ferrocyanide acidified with dilute sulphuric acid, with decinormal potassium permanganate. The fixed-potential half-cell should contain a solution of the ferricyanide acidified with dilute sulphuric acid.

Difficulty will have been experienced in the above exercises in finding the end-point owing to the movement of the galvanometer gradually approaching zero. In the following method

the end-point is more accurately determined by finding the position of a sharp rise in the potential of the titrated mixture. Provided that the oxidising liquid being added has a standard potential differing sufficiently from that of the system being titrated, a sharp rise in potential will be obtained as soon as the former is present in excess. The position of this rapid rise will therefore mark the end-point of the titration.

Exercises (3) *and* (4).—Repeat the titrations in Exercises (1) and (2) above, using a method similar to that described under (2) on p. 193. Any fixed-potential half-cell may be employed, and this half-cell is connected to the positive end of the potentiometer wire.

The results of the two electrometric methods may now be compared. Such methods are especially of value where the colour of the liquid prevents the use of any indicator. For example, potassium ferrocyanide may be estimated in the presence of Prussian blue by an electrometric method.

Reduction-Oxidation Titration with the use of Indicators

Those oxidising agents which have themselves a pronounced colour, and which give on reduction a solution which is colourless, serve as indicators in themselves. But in many cases the addition of another substance is necessary for this purpose. Such substances fall into two classes. In one class the indicator is capable of oxidation to a substance of a different colour, the process being irreversible. The use of such an indicator, diphenylamine, has been described under the titration of a ferrous solution by potassium dichromate (p. 120). It is clear that the substance used as an indicator must be less easily oxidised than the substance which is being titrated. In the case of diphenylamine the potential at which a marked colour change occurs is 0·76 volt in acid solution. This is almost identical with that of the standard potential of the ferrous-ferric system. It is therefore necessary, if a satisfactory end-point is to be obtained, to add some substance such as a phosphate or a fluoride to reduce the concentration of the ferric ions.

In the other class of indicators are substances which form one side of a reduction-oxidation equilibrium, in which the

reduced and oxidised systems have different colours. The laws which govern the equilibrium in each of these systems are the same as in the case of other reduction-oxidation systems. When present in small amount the indicator system adjusts itself to that ratio between the concentrations of its reduced and oxidised states which corresponds to the potential of the solution in which it is, each such adjustment being accompanied by a change in colour. The most marked change will occur when the potential of the liquid undergoing titration rises rapidly owing to the presence of a slight excess of the titrant, provided that the standard potential of the indicator redox system lies within the range covered by this rapid rise.[1] A difference of 0·1 volt is sufficient to change the indicator system from a point at which 90 per cent. is in the reduced form to one at which 90 per cent. is in the oxidised form, such a change being accompanied by the maximum perceptible alteration in colour.

Many indicators have been found which are suitable for use in reduction-oxidation titrations. As an example, *o*-phenanthroline ferrous sulphate may be cited. This indicator has an intense red colour in the reduced state, and a faint blue colour in the oxidised condition, its standard redox potential being in the region of 1·1 volt. Hence it is suitable for use in the titration of ferrous ions by ceric sulphate or by potassium dichromate, either of which reagents has a standard potential exceeding 1·1 volt, while the standard potential of the ferrous-ferric system is so far below this value that the addition of a substance such as a phosphate to suppress the concentration of the ferric ions is unnecessary. The use of *o*-phenanthroline as an indicator has already been described under the determination of ferrous iron by ceric sulphate, p. 135.

CONDUCTOMETRIC ANALYSIS

The conductivity of a solution of an electrolyte depends not only on the number of ions present in unit volume, but also upon their speed or mobility. Hydrogen ions and hydroxyl ions are by far the most mobile, the mobility of the hydrogen ion being the greater. Other ions, though differing from each

[1] Compare this proviso with that governing the selection of indicators for acidimetry titrations, p. 65.

other in mobility, do so to a much smaller degree. Hence any process which diminishes the number of ions present, or substitutes for hydrogen or hydroxyl ions, some other ion of less mobility, lessens the conductivity of the solution and *vice versa*. For analytical purposes it is not usually necessary to determine the specific conductivity of a solution but merely to follow changes in the conductivity as one reactant is added to the other. The method may therefore be applied to neutralisation processes, to certain precipitation processes and even to reduction-oxidation processes if a marked change in the hydrogen ion concentration occurs. It possesses advantages over the ordinary titration methods where the colour of a solution masks that of the indicator, and in some cases gives better results than potentiometric methods. The conductivity method can be used under suitable conditions for titrating very dilute solutions, *e.g.* 0·0001 N, and it is practically the only method for the titration of a weak base by a weak acid.

Consider, for example, the titration of a strong acid by means of a strong alkali. The solution at first contains the very mobile hydrogen ion, and therefore the conductivity is high. As the alkali is run in, the added hydroxyl ions combine with the hydrogen ions, which are therefore gradually replaced by the less mobile alkali metal ion, the water formed being practically unionised. The conductivity will therefore become less on this account, even neglecting the small increase in the volume of the solution. After the end-point of the titration the additional alkali is no longer neutralised, so that, provided a fairly concentrated solution of alkali is used, there is a rapid increase in the concentration of ions present, one of which is the very mobile hydroxyl ion. The result is a rapid increase in the conductivity of the solution.

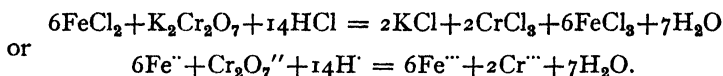
If the burette readings obtained in such a titration are plotted against the reciprocal of the resistance of the solution as horizontal and vertical co-ordinates respectively, a V-shaped curve is obtained, and the true end-point can be found from the point of intersection of the two straight lines. A reading need not therefore be made at the end-point; in fact, only three readings before and three after the end-point are necessary, provided that the conditions are so chosen that the readings are represented by two virtually straight lines. This will not be the case if there is a change in the conductivity due to a

considerable increase in volume on adding the liquid from the burette. For this reason the concentration, expressed as normality of the added liquid, should be at least ten times that of the liquid being titrated. This involves titrating rather large volumes of liquid if a 50 ml. burette is to be used, but this can be avoided if a micro-burette is available.

There are many applications of the conductometric method in analytical chemistry. In addition to various neutralisation processes it can be applied to precipitation processes, since there is a sudden increase in the conductivity of the solution being titrated after the point of equivalence, as ions are then no longer removed from solution. Therefore, provided that a concentrated solution of the reagent in the burette is used there is a fairly sharp break in the conductivity-volume curve at the point of equivalence. The shape of the curve in this case will be a nearly horizontal line up to the point of equivalence, followed by a line inclining upwards. The conductivity method can also be applied to reduction-oxidation titrations in which hydrogen ions take part, *e.g.* in the oxidation of a ferrous salt by potassium dichromate

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 6FeCl_3 + 7H_2O$$

or

$$6Fe^{\cdot\cdot} + Cr_2O_7'' + 14H^{\cdot} = 6Fe^{\cdot\cdot\cdot} + 2Cr^{\cdot\cdot\cdot} + 7H_2O.$$

The disappearance of the hydrogen ions will cause a fall in the conductivity until the reaction is complete, after which on further addition of potassium dichromate it will remain almost constant.

Since a direct current would electrolyse the solution under investigation, and polarise the electrodes, it is usual to employ an alternating current in conjunction with a Wheatstone bridge. A telephone may be used to determine the balance of the resistances in the bridge, or the alternating current passing through the solution may be rectified by a valve or crystal detector and measured. (For an account of this latter method, see Callan and Horobin, *J.S.C.I.*, 1928, 329 T.) A telephone is used in the apparatus described below.

To obtain accurate results it is necessary to use an alternating current of high frequency, *e.g.* several thousand cycles per second. High-frequency currents can be generated by

means of a suitable induction coil, a wireless valve, or other type of oscillator, but it is possible by using a simple "step down" transformer supplied by current from the A.C. mains (usually 50 cycles per second) to obtain results sufficiently accurate for studying the principles of conductometric analyses, These inexpensive transformers are used for working electric bells or lighting small electric lamps, the output being between about four and eight volts. They possess the advantage over the commonly used induction coil of being almost silent in action.

The telephone to be used for determining the balance of resistance in a Wheatstone bridge (*i.e.* in place of the galvanometer) should have a resistance of between 10 and 30 ohms, the ordinary wireless headphones having far too high a resistance. It is advisable to make one connection of the low voltage A.C. supply to the calibrated wire of the bridge, as

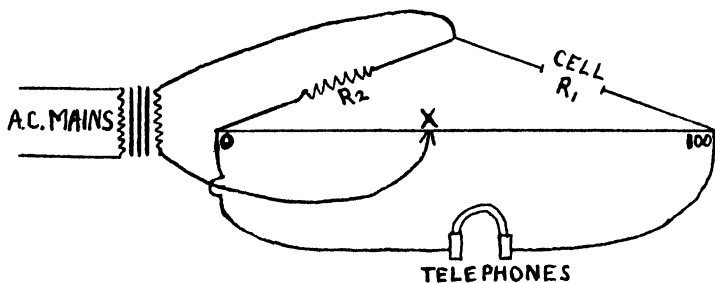



FIG. 37.

this ensures that maximum current passes through the relatively poor contact between the sliding knife-edge and the wire (see Fig. 37).

The conductivity cell can be made out of a very wide mouthed bottle or glass jar of between 75 and 100 ml. capacity, if a 5 ml. micro-burette is available for the titration. If, however, an ordinary 50 ml. burette must be used the cell should have a capacity of 120 to 150 ml. A suitable bung is bored with four holes along a diameter and another hole for a stirrer. The four holes are so placed that by inserting the electrodes in any two of them the distance between the electrodes can be varied to a considerable extent according to the conductivity of the solution being titrated. The two

free holes are fitted with a thermometer and the burette to be used. The stirrer can be made from a glass rod, onto one end of which is fused a short piece of rod at right angles. The ends of the latter are flattened and bent at an angle to agitate the liquid. The upper end of the rod is connected by means of pressure tubing direct to a small electric motor held in a clamp. The end of the stirrer should almost touch the bottom of the bottle, leaving room for the electrodes to be completely immersed in the liquid above the level of the stirrer vanes. Alternatively, stirring may be effected by means of a current of air. The cell is placed inside a suitable vessel to act as a water-jacket for maintaining the temperature as constant as possible. The electrodes are made of platinum foil (0·15 mm. thick) and to obtain a satisfactory reading of the balance point on the bridge it is necessary to deposit a thin coat of platinum black on both of them, as described below. This reduces polarisation and greatly diminishes noise in the telephone at the balance point. Two pieces of platinum foil about 1 square centimetre each are rubbed with fine emery paper and welded to two pieces of platinum wire 1·5 cm. long and 0·4 mm. in diameter. The welds are easily effected by heating the metal in a blowpipe and hammering the hot wire onto the hot foil resting on an iron block. The free ends of the platinum wires are then fused into glass tubes which will just slide in the holes in the bung, and a little mercury is placed in each tube to make contact with the platinum wire. Before depositing platinum black on the electrodes, they must be immersed in warm chromic acid mixture (p. 47) for at least ten minutes and then washed in distilled water. Transfer them to a small beaker nearly filled with a solution containing 3 grams of platinic chloride and 10 ml. of dilute hydrochloric acid in 100 ml. of solution. Connect both electrodes to the negative pole of a lead accumulator, and the positive pole of the latter to another piece of platinum foil and immerse this also in the beaker. As soon as the cathodes are completely covered with a black deposit, remove and wash them in distilled water, in which they should be kept until ready for use. When required for use the electrodes should be mounted in the bung so that they are opposite and parallel to each other, and it is important that they should be rigid enough to prevent any relative motion during a titration.

Exercise 1.—**Titration of Sodium Hydroxide with Hydrochloric Acid**—If a 5 ml. micro-burette is available for delivering the acid, measure 50 ml. of N/100 sodium hydroxide into the smaller cell. If an ordinary 50 ml. burette must be used, measure out 100 ml. of the alkali into the larger cell. Fit the bung carrying the stirrer and the electrodes spaced well apart, since the conductivity in this case will be fairly high. Make sure that the electrodes are completely covered, adding more water if necessary, and insert the thermometer and the tip of the burette containing 0·2N hydrochloric acid through the free holes in the bung. Add water to the outside vessel, which must also be supplied with a thermometer. Run the motor driving the stirrer in the cell slowly and, if necessary, adjust the temperatures of the cell and the jacket to that of the room. Connect the cell to the other components of the Wheatstone bridge as indicated in the diagram. About 100 ohms should be a suitable value for the fixed resistance R_2. Determine the point on the bridge where the sound in the telephone is at a minimum. Make a note of the reading and run in exactly 0·5 ml. of the acid if using a micro-burette, or exactly 1 ml. of acid if using an ordinary burette. When the stirrer has mixed the contents of the cell, again determine the null point on the bridge. The conductivity will be found to have fallen owing to the removal of hydroxyl ions. Make further additions of the same volume of acid until at least three readings are obtained after the equivalence point is passed as indicated by a rise in the conductivity due to the presence of the rapidly moving hydrogen ions supplied by the excess of acid. The temperature of the liquid in the cell should not be allowed to rise more than 1° C. (corresponding to a change in the conductivity of about 2 per cent.), the outer jacket being cooled if necessary.

Calculate the value of the resistance of the cell from the equation $R_1 = R_2 \frac{(100-x)}{x}$,

where R_1 = the resistance of the cell,

R_2 = the selected fixed resistance in the bridge,

x = the length of wire between the zero end and the point X, where a balance is obtained.

Plot the reciprocals of R_1 against the volume of acid added, join the points, and determine the point of intersection of the two lines which gives the volume of the acid equivalent to the alkali taken. Titrate the same volume of alkali, using phenolphthalein as indicator, and compare the result with the conductometric method.

Exercise 2.—**Titration of Ammonium Hydroxide by Acetic Acid**—This is an instance of the special value of the conductometric method, since the titration of a weak base by a weak acid is not practicable with an indicator, owing to the small rate of change in the *p*H at the stoichiometric point. There is, however, a sufficiently marked break in the conductivity curve to locate this point. If a 5 ml. micro-burette is available, measure out 50 ml. of an approximately N/50 ammonium hydroxide solution into the smaller cell and titrate this with an approximately N/2 acetic acid solution as described in Exercise 1, or if an ordinary 50 ml. burette is used, take 100 ml. of the ammonium hydroxide. The concentration of the ammonium hydroxide and the acetic acid can be checked by titration with standard hydrochloric acid and sodium hydroxide respectively.

Exercise 3.—**Titration of a Ferrous Salt by Potassium Dichromate**—For the smaller cell, used in conjunction with a 5 ml. micro-burette, take 50 ml. of approximately N/10 ferrous ammonium sulphate made up in 0·7N sulphuric acid, or 100 ml. of this solution for the larger cell, and titrate with an almost saturated solution of potassium dichromate.

Exercise 4.—**Titration of Sodium Chloride by Silver Nitrate**—For the smaller or larger cell take 50 or 100 ml., respectively, of N/20 sodium chloride, and titrate with normal silver nitrate.

PART III

GRAVIMETRIC ANALYSIS

IN the gravimetric method of analysis, the determination of weight is the principal quantitative measurement involved. Although, as a general rule, the procedure is less simple and the manipulation more difficult than in volumetric analysis, this is not necessarily the case. In order to determine, for example, the amount of zinc in a sample of basic zinc carbonate, a weighed quantity of the substance is heated in a crucible to dull redness until it is converted into zinc oxide. The weight of the zinc oxide is then ascertained, and, as the composition of the oxide is known, the percentage of zinc in the basic carbonate is easily calculated from the weight of the oxide obtained. It is obvious, however, that the result will not be correct unless the residue consists of zinc oxide only.

When a complete analysis of a complex substance is required, the analytical process is less simple, and it has already been stated that, as a rule, the constituents of the substance must be separated from one another before the amount of each can be ascertained. The separation is usually accomplished by precipitating each constituent in the form of an "insoluble" compound, which is then filtered, washed, dried, and weighed. The attainable accuracy of the analysis depends mainly on the insolubility of the precipitate, on the completeness of its separation from the other substances present, and on its composition at the time of weighing being perfectly definite and known.

One of the most difficult problems met with in quantitative analysis is the selection of good methods of separation. A perfect separation is rarely obtained by the methods adopted in qualitative analysis; these methods are often quite unsuitable, or require modification, for the purposes of quantitative analysis. The separation of iron and magnesium, for example, by means

of ammonium chloride and ammonia, is imperfect. All the iron is precipitated as ferric hydroxide, but, even in presence of a large excess of ammonium chloride, the precipitate always contains more or less magnesium hydroxide. In order to separate the co-precipitated magnesium, the ferric hydroxide, after it has been filtered and washed, is dissolved in acid, and ammonium chloride and ammonia are again added to the solution. After filtering the ferric hydroxide, it may be necessary to dissolve it again and to precipitate it a third time before the separation of the iron and magnesium is complete. The several filtrates are then combined and the magnesium in solution is precipitated as magnesium ammonium phosphate.

It is evident, from the foregoing, that precipitation and filtration form an important part of the routine of gravimetric analysis. The general description of these operations is given in Part I., pp. 30 to 37, whilst some of the apparatus and processes peculiar to gravimetric analysis are described in the following pages.

NOTES ON APPARATUS

(*See also p.* 16)

Porcelain Crucibles.—For most ordinary purposes, crucibles of good porcelain, 3 to 4 cm. in diameter, are suitable. Before being exposed to a high temperature, porcelain crucibles should be carefully heated with a small flame in order to avoid fracture. Porcelain crucibles must not be used for substances that are to be treated with hydrofluoric acid, or for fusions with sodium hydroxide, sodium peroxide, or alkali carbonates ; and they are not so suitable as platinum crucibles for substances that require heating to a very high temperature. Porcelain crucibles may be permanently marked, for the purpose of identification, by writing in ink a distinctive letter on each crucible and lid, drying the ink by gently warming, applying more ink, and finally heating the porcelain to bright redness, so as to burn the residual ferric oxide into the glaze.

Silica Crucibles.—Although probably more fragile than porcelain crucibles, silica crucibles may be safely exposed to sudden changes of temperature without any risk of fracture. Silica vessels must not be used for alkalis or hydrofluoric acid.

Platinum Crucibles.—When the use of a platinum crucible is admissible, it is usually preferable to one of porcelain. Platinum crucibles can be more readily and more uniformly heated to redness than porcelain crucibles. On account of the expense of platinum, however, it is often necessary to restrict the use of platinum vessels to cases where they are indispensable. *The following rules and precautions with regard to platinum vessels must be observed*:—

1. Platinum crucibles must not be exposed to a luminous flame, since this will cause the metal to lose its lustre and to become brittle—owing, probably, to the formation of a carbide of platinum.

2. Compounds of lead, silver, zinc, tin, bismuth, arsenic, and antimony must not be heated in platinum crucibles when there is any possibility of reduction to the metallic state, as the metals, having comparatively low melting-points, may alloy with the platinum.

3. Great care should be taken in igniting phosphates in platinum crucibles, since the presence of reducing substances, such as charred filter paper, may result in the formation of traces of phosphorus which, combining with the platinum, renders it brittle. It is safer to use a porcelain crucible for phosphates.

4. Platinum crucibles must not be used for fusions with hydroxides, nitrates, nitrites, and cyanides of the alkalis.

5. Evaporations or fusions in which chlorine, bromine, or iodine is set free must not be performed in platinum vessels. This rule applies to mixtures in which both chloride and nitrate are present: and to ferric chloride in the presence of concentrated hydrochloric acid.

6. Care must be taken to avoid damaging a platinum crucible and causing indentations by dropping it on the bench. It must on no account be squeezed with the object of loosening the solidified cake after a sodium carbonate fusion.

7. Platinum ware should be kept scrupulously clean. Adhering substances or stains can sometimes be removed by boiling a little concentrated hydrochloric acid in the crucible, or by fusing a little potassium bisulphate[1] in the crucible and removing the salt by means of boiling water. The crucible should then be polished with fine, moist sea sand, which is

[1] This salt when fused attacks platinum to a slight extent.

gently rubbed on the surface of the metal with the finger. After polishing, the platinum should be rinsed with distilled water and dried.

Triangles.—A very satisfactory form of pipe-clay or porcelain triangle, on which a crucible is placed during the process of heating, is shown in Fig. 38. For the usual sizes of crucibles, triangles with sides 5 cm. or 6½ cm. long are suitable. Nickel wire is preferable to iron wire on account of its much greater durability. A silica triangle may be used, except with a platinum crucible, to which it tends to adhere owing to the reducing action of the flame.

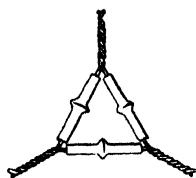



FIG. 38.

Perforated Silica or Asbestos Screens.—It is often important to exclude flame gases from the interior of a crucible during an ignition, and, for this purpose, the device shown in Fig. 39 may be used. It consists of a silica plate, 13 cm. square, in which is cut a round opening large enough to admit the crucible to two-thirds of its depth. The plate is held in an inclined position by means of a clamp. A higher temperature in the crucible may be reached by using a silica plate with a larger opening, and placing over the latter a disc of platinum in which a hole is cut to fit the crucible. Instead of a silica plate, a sheet of asbestos may be used.

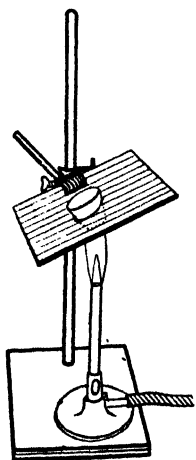



FIG. 39.

Crucible Tongs.—Crucible tongs should be made of brass or of gun-metal, and it is an advantage to have them fitted with platinum tips or the tips covered with thin platinum foil, secured by platinum wire. A useful substitute is a small pair of iron pliers, which may be used for a platinum crucible if platinum tipped tongs are not available. All tongs must be kept scrupulously clean.

The Gooch Crucible

Filtration by means of a Gooch crucible is frequently advantageous, and is a most convenient method of collecting a precipitate directly in the crucible in which it is finally weighed. A porcelain Gooch crucible of the size and shape shown in Fig. 40 is suitable for most purposes. The bottom of the crucible is perforated with a number of small holes. The crucible, which is always used in conjunction with the filter-pump, is fitted into a glass adapter by means of a narrow rubber ring (cut from a piece of rubber tubing, 2½ cm. in

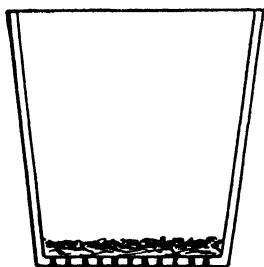



FIG. 40.—Section of Gooch Crucible (Actual Size).

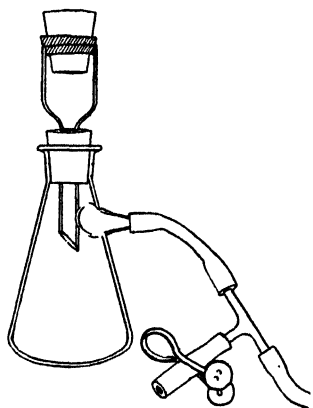



FIG. 41.

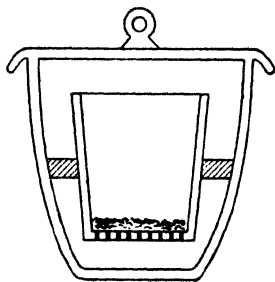
diameter), and the adapter passes through the rubber stopper of a filter-flask. The filtering medium is fine, white, anhydrous asbestos, and a special quality is sold for the purpose.

Preparation of the Asbestos Filter.—Connect the filter-flask, fitted with the adapter supporting the crucible, to the filter-pump (Fig. 41). In using a Gooch crucible, it is most important that the filtration should not be conducted under too great a pressure, and, to prevent this, the connection with the pump should include some means of regulating the pressure, such as that described on the next page.

Place a very thin layer of wetted glass wool in the bottom of the crucible, pressing it down and taking care that no fibres are sticking up round the edges. Shake about 0·05 gram of the asbestos with 25 ml. of water and pour about 20 ml. of the

mixture into the crucible. Allow the water to drain, using very gentle suction. Then turn on the maximum pressure the regulator will allow. Add the remainder of the asbestos and wash the filter with about 100 ml. of warm water. If the filter is properly prepared with suitable asbestos, 100 ml. of water will pass through in about one minute under a pressure equal to that of 5 cm. of mercury.

FIG. 42.

Place the crucible on a watch-glass and dry it for an hour in an air-oven at a temperature about 20° higher than that required for the precipitate that is subsequently to be collected in the crucible. If the precipitate requires ignition, place the crucible within a larger platinum crucible (or a nickel crucible, fitted with an asbestos ring, as shown in Fig. 42), and heat the larger crucible with the flame. Cool the Gooch crucible in a desiccator, and weigh it. It is then ready for use.

Pressure Regulator for Use with the Filter-Pump.—Some means should always be used of limiting the maximum pressure under which filtration by means of the filter-pump is conducted, and the following arrangement is simple and effective.

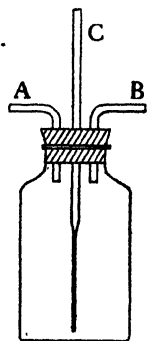



FIG. 43

Three tubes pass through a rubber stopper fitted into a bottle (Fig. 43). A and B are connected to the filter-pump and to the filter-flask, respectively. The tube C is drawn out to form a capillary at its lower end and forms an air-leak. The size (or length) of the capillary is adjusted by trial, so that, when the pump is working at full power, the pressure in the bottle when B is closed cannot fall below a definite value, viz., about 5 cm. of mercury less than atmospheric pressure. The adjustment is easily made with the help of a simple pressure gauge; a piece of glass tubing bent into a U-form and containing mercury is suitable for the purpose.

The bottle also safeguards the contents of the filter-flask from contamination with water from the filter-pump, should the water-pressure momentarily fail.

The Sintered Glass Crucible

In this the filtering medium, instead of asbestos fibre, is a fixed layer of sintered glass particles. These crucibles (Fig. 44) can be obtained in widely varying grades of porosity. If not used for strongly alkaline liquids, they remain constant in weight for long periods. They can be heated to about 400° in an air-bath. Being ready for immediate use, and of an approximately known weight, they are more convenient than an ordinary Gooch crucible. They are used in conjunction with a filter-pump.

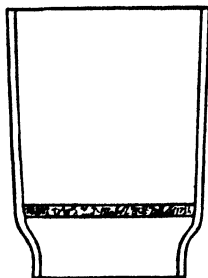



FIG. 44.

The Rose Crucible

When it is necessary to ignite a precipitate in an atmosphere of hydrogen,[1] carbon dioxide, or oxygen, a Rose crucible is used. The crucible, its cover, and the tube through which the gas is led into the crucible (all of porcelain or silica) are shown in Fig. 45.

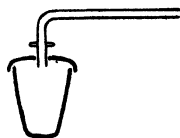



FIG. 45.

THE IGNITION AND WEIGHING OF PRECIPITATES

After a precipitate has been filtered and washed, it requires further treatment before it can be weighed. In the first place, if a filter paper has been used it must be destroyed by incinerating it either in presence of the whole precipitate or after separating the precipitate from it. The precipitate, together with the filter ash, is then " ignited " in a weighed crucible. (The terms " ignite " and " ignition " are commonly used in analytical chemistry, and refer to the process of heating a substance to a high temperature, without allowing the direct access of the flame to the substance.) The purpose of the ignition is (1) to dry or dehydrate the precipitate completely, and, in many cases, (2) to convert the precipitate, which may

[1] It is essential before starting the ignition to be sure that the hydrogen is not mixed with air. For the preparation of these gases, see Appendix, p. 476.

be of uncertain composition, into another compound of definite and known composition. Copper, for example, may be precipitated as hydrated copper oxide, CuO, xH_2O, which is ignited and weighed as anhydrous cupric oxide, CuO; and zinc may be precipitated as basic carbonate which is of variable composition but is easily converted by ignition into zinc oxide, ZnO. The weight of the ignited precipitate is then ascertained by weighing the crucible and its contents, and deducting the weight of the crucible and that of the filter ash (unless the latter is negligible) from the total weight.

The ignition is performed by heating the crucible containing the precipitate with the flame of a Bunsen burner, a Méker burner, or a blowpipe, according to the temperature required.

The Bunsen Burner.—A good Bunsen burner, giving a flame of medium size, should be used for heating purposes.

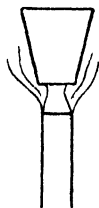



FIG. 46.
Incorrect Position of Crucible in Bunsen flame.

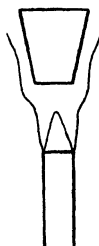



FIG. 47.
Correct Position of Crucible in Bunsen flame.

In order that it may be possible to obtain suitable non-luminous flames of different sizes, it is most important that the air-regulator of the burner should be in working order; it seldom happens that the mere lighting of the burner, without carefully adjusting the air supply, gives the best flame for a given purpose.

When a Bunsen burner is used for strongly heating a crucible, rather more air than is just required to produce a non-luminous flame should be admitted by means of the regulator; too much air, however, gives a noisy flame, which is unsuitable. The position of a crucible in a Bunsen flame is important. If the crucible is placed so near the burner that the inner cone of unburnt gas impinges on it (Fig. 46), the bottom of the crucible will not become properly heated. Again, the crucible must not be enveloped in a large flame

burning with a restricted air supply. The proper position, in which the bottom of the crucible is about half an inch above the top of the inner cone, is shown diagrammatically in Fig. 47. In order that the position of the crucible in the flame may be easily adjusted, the pipe-clay triangle on which the crucible rests should be supported on a movable retort-stand ring.

The Méker Burner.—When a Bunsen flame is fully aerated, the volume of air passing into the burner is about 2·5 times the volume of the gas, whereas for the complete combustion of one volume of coal gas about six volumes of air are required. If a mixture of gas and air in the latter proportions were

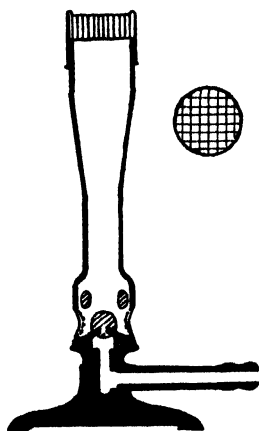



FIG. 48.

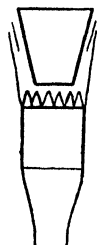



FIG. 49. Correct Position of Crucible in Méker flame.

lighted at an ordinary burner, the flame would "strike back" and burn at the bottom of the tube.

In the Méker burner, the holes for the admission of air are large enough to pass sufficient air for the complete combustion of the gas, and a nickel grid is fitted into the top of the burner in order to prevent the flame striking back (Fig. 48). The flame of a Méker burner is smaller, and therefore hotter, than a Bunsen flame burning the same amount of gas, and the cold centre of unburnt gas is entirely absent. The hottest part of the flame is close to the nickel grid, but the temperature of the flame is much more uniform than that of a Bunsen flame. For igniting precipitates it is seldom necessary to use a blowpipe if a Méker burner is available.

Drying the Precipitate and the Filter

It is often necessary to dry the precipitate and the filter before the latter is incinerated. To do this, first remove the water in the stem of the funnel by means of filter paper; cover the mouth of the funnel with a piece of paper, the latter being folded over the rim of the funnel so that each fold overlaps the preceding one; and then place the funnel in the steam-oven in an upright position, and leave it there for several hours until the precipitate and paper are dry.

Incineration of the Filter

In certain cases, the filter may be incinerated in presence of the whole precipitate; in others, the precipitate must be detached as far as practicable from the filter before the latter is incinerated. The procedure depends on the nature of the precipitate.

The filter must be incinerated apart from the precipitate (1) if the precipitate is fusible or volatile at the temperature of incineration, *e.g.* silver chloride, or (2) if the precipitate suffers reduction to the metallic state during the charring of the filter paper, *e.g.* silver chloride, lead sulphate, zinc carbonate, or (3) if the compound that is to be weighed is decomposed at the high temperature of the incineration; *e.g.* if calcium oxalate is to be converted into calcium carbonate, it must not be heated above dull redness.

The filter may be incinerated in presence of the precipitate in the case of (1) silica; (2) the oxides of iron, aluminium, chromium, and manganese; and (3) the sulphates of barium, strontium, and calcium.

The incineration is performed in a porcelain crucible, or in a platinum crucible if the use of the latter is permissible (see p. 210).

Tare of the Crucible.—Place the clean crucible, covered with the lid, on a pipe-clay triangle, and heat it to redness for a few minutes with a properly adjusted Bunsen flame. Remove the flame, and after about a minute lift the lid of the crucible with tongs, and place it temporarily on the desiccator cover, which is held inverted in the left hand; then transfer the crucible and finally the lid to the desiccator. (Except on the ground rim, the desiccator cover must, of

course, be free from grease.) Allow the desiccator to remain in the balance-room for twenty to thirty minutes, then weigh the crucible and lid, and afterwards replace them in the desiccator. After the crucible has been heated and weighed it must not be placed directly on the bench, but only on the pipe-clay triangle, in the desiccator, or (when cold) on a sheet of clean paper.

Incineration of the Filter in Presence of the Precipitate

When this method is applicable, it is not necessary to dry the precipitate in the steam-oven; but large precipitates of chromic, ferric, and aluminium hydroxides should be partially dried as described on p. 217, before proceeding with the incineration.

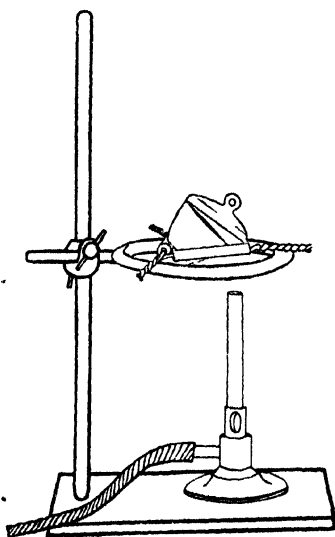



FIG. 50.

Detach the filter very carefully from the funnel by means of a small spatula and remove it from the funnel. Fold the filter paper so as to form a small packet enclosing the precipitate, care being taken not to tear the paper. Place the packet in the weighed crucible and press it down gently. Remove any trace of the precipitate adhering to the funnel with a piece of "ashless" filter paper — first moistening the funnel, if necessary, by breathing into it—and drop this piece also into the crucible. Place the crucible on a pipe-clay triangle in a slanting position and cover it partially with the lid, which should rest partly on the triangle, as shown in Fig. 50.

Place a small (2 cm.) flame under the crucible lid and about 2½ cm. from it, as shown in the figure. The hot gases are deflected into the crucible, and the contents soon become dry. When the paper begins to char, remove the lid of the crucible and place it meanwhile on a glazed tile or a watch-glass. Place the crucible upright, and adjust the size of the

flame and the distance of the crucible from it, so that the paper gradually chars without taking fire. If the paper should take fire, remove the flame and cover the crucible with the lid for a moment. When the escape of vapour ceases and the charring of the paper is complete, place the crucible *in a sloping position* again and heat more strongly until all the carbon is oxidised. If the carbon burns with difficulty, the oxidation may be accelerated by shifting the crucible into various sloping positions, so that all parts that are blackened with carbon may become properly heated. A deposit of carbon is sometimes found on the under surface of the crucible lid, but this is easily removed by heating the inverted lid with the flame.

The precipitate is now ready for ignition, and the special instructions given for each should be followed. After igniting, remove the flame, wait for about a minute, then place the crucible in a desiccator and allow it to cool for twenty to thirty minutes. Weigh the crucible with its contents.

The ignition must be repeated as often as may be necessary until constant weight is attained. By "constant weight" is here meant that the difference between two consecutive weights is not more than two-tenths of a milligram, *i.e.* 0·0002 gram. The weighing must be performed as quickly as possible, especially if the precipitate is hygroscopic, and, when a weighing is repeated, all the weights used in the previous weighing should be placed on the balance before the crucible is removed from the desiccator. It is a mistake to leave an ignited precipitate in a desiccator for a long time, *e.g.* overnight, before weighing it; it should be re-ignited, and then weighed after cooling for not more than about thirty minutes.

Incineration of the Filter apart from the Precipitate

The precipitate and filter must be dried as far as possible in the steam-oven. Two sheets (about 25 cm. square) of glazed paper[1]—white if the precipitate is coloured, and black if the precipitate is white—are laid on the bench. A shallow porcelain basin, about 5 cm. in diameter, or a watch-glass of the same size, is placed on one of the sheets. The Bunsen burner or other metal apparatus, from which particles of rust or dirt are

[1] The glazed paper must have clean-cut edges and be free from creases, and should be kept flat and unfolded between two pieces of cardboard.

liable to drop, must not on any account be placed on the glazed paper.

Remove the well-dried filter from the funnel. Hold the filter over the glazed paper and loosen the precipitate by gently pressing the cone-shaped filter with the fingers. Transfer the bulk of the precipitate very carefully to the basin or watch-glass. Carefully unfold the filter and loosen the precipitate still adhering to it by lightly rubbing with the paper itself, care being taken, however, not to rub off any paper fluff. Empty this portion of the precipitate into the basin, then place the latter on the second sheet of paper, and cover the basin meanwhile with a clock-glass.

Fold the filter paper into a narrow strip, as shown in A to D (Fig. 51), the shaded portion in A representing the soiled

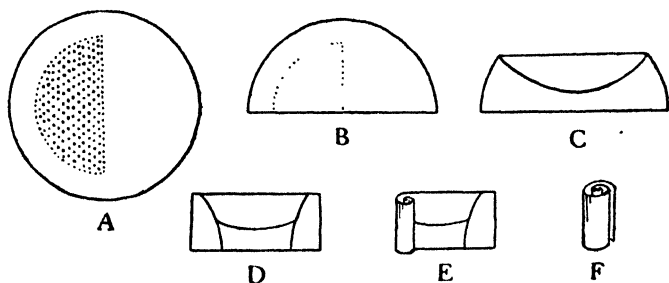



FIG. 51.

part of the paper, which is inside after folding as in B. Carefully wipe off any traces of the precipitate adhering to the funnel by means of the paper strip—first breathing into the funnel in order to moisten it—and then wrap up the strip into a compact roll, as shown in E and F. Place the roll in the weighed crucible which, meanwhile, is left in the desiccator.

If any precipitate has been allowed to fall on the glazed paper, transfer it very carefully to the basin by bending, but not folding, the sheet, and sweeping the particles into the basin by means of a small brush.

Now place the open crucible containing the filter on a pipe-clay triangle, and incinerate the filter in the manner described on p. 218. Allow the crucible to cool, and then treat the filter ash in accordance with the instructions given for the particular precipitate (see, for example, silver chloride

or copper oxide). When the crucible is cold again, place it on the glazed paper, and very carefully transfer the main part of the precipitate to the crucible. Finally, dry or ignite the precipitate in the manner specified, and repeat the process until constant weight is attained.

Weighing Precipitates without Ignition

(1) **Use of Tared Filter Paper.**—Occasionally it is necessary to weigh on the filter paper a precipitate which would be decomposed by ignition, and for which a Gooch or sintered glass crucible would not be suitable. In such a case the paper before use is folded as usual for insertion in a funnel, the apex then doubled back, and the paper rolled into cylindrical form. This is then placed in a weighing-bottle, and dried at 105°—not in a steam-oven [1]—until constant in weight. After filtration and washing, the filter is first dried in the funnel in a steam-oven, then transferred to the weighing-bottle, and the drying completed at 105°.

(2) **Use of Acetone in Drying Precipitates.**—In certain cases, when the composition of the precipitate after simple drying is known, ignition may be avoided and the time of procedure much shortened, by using a Gooch or sintered glass crucible, and, after washing the precipitate as directed to get rid of the salts in solution, continuing the washing with acetone. The inside walls of the crucible and the precipitate are well rinsed about five times with 5 ml. portions of acetone, air drawn through the filter for a few minutes, and the drying finished in a vacuum exsiccator, or by placing for a few minutes in a steam-oven, or low temperature air-oven. Among the precipitates suitable for this treatment are barium sulphate, mercuric sulphide, the halides of silver, lead sulphate, calcium oxalate (CaC_2O_4, H_2O), and magnesium ammonium phosphate ($MgNH_4PO_4, 6H_2O$).

[1] Filter paper retains some moisture if heated in an ordinary steam-oven, the temperature of which is below 100°. Air-ovens which are thermostatically controlled are useful for many drying operations.

Typical Gravimetric Exercises

THE following section contains a number of simple exercises which have been so selected that they involve all the more important manipulative operations of gravimetric analysis. Each exercise can be performed with a salt which is readily obtainable in a state of purity, and the experimental result can therefore be checked by calculation. It may be preferred, however, to perform the analyses with solutions or solids of "unknown" composition. A list of solutions that are suitable for this purpose, with particulars as to their preparation, is given in the Appendix.

Most of the exercises given in this section should be carried out before the analyses described in later sections of the book are attempted. The exercises are arranged roughly in order of difficulty, except that, for convenience in description, the determination of aluminium has been placed immediately after that of iron, although it presents more difficulty than many of the other exercises.

Determination of Water in Magnesium Sulphate Heptahydrate

OUTLINE OF METHOD.—A weighed quantity of the magnesium sulphate is heated to dull redness, and the loss of weight, which represents the water, is ascertained.

Procedure.—Heat a crucible and lid with a full Bunsen flame for five minutes. Remove the flame, allow the crucible to cool for about a minute, and then place it in a desiccator for half an hour. Weigh the crucible and lid accurately. Place about 0·6 gram of magnesium sulphate, $MgSO_4 , 7H_2O$, in the crucible, and weigh again. Place the covered crucible resting on a pipe-clay triangle, about 15 cm. above a small flame (not more than 2½ cm. high). At intervals of a few minutes, lower the crucible and increase the flame gradually until the bottom of the crucible is heated to dull redness. Maintain the crucible at this temperature for about ten minutes.

Allow the crucible to cool in a desiccator for half an hour, and weigh. Repeat the heating process until constant weight is attained.

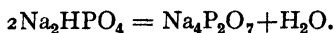
From the loss of weight, calculate the percentage of water in magnesium sulphate heptahydrate.

Determination of Water in Barium Chloride Crystals

Weigh accurately in a tared porcelain crucible 1·5 to 2·0 grams of barium chloride crystals, $BaCl_2, 2H_2O$. Heat the crucible and contents to a temperature *not exceeding dull redness* until constant weight is attained (compare previous exercise). From the loss of weight, calculate the percentage of water in the barium chloride crystals.

Determination of Anhydrous Disodium Hydrogen Phosphate in the Crystalline Salt

In a tared porcelain crucible weigh accurately about 0·5 gram of sodium phosphate, $Na_2HPO_4, 12H_2O$ (selected crystals free from efflorescence). Heat the crucible and contents for about an hour in the steam-oven, and then at a gradually increasing temperature with a Bunsen flame. Finally, ignite at a red heat for about ten minutes. Cool, and weigh. Repeat the ignition until constant weight is attained. The residue is sodium pyrophosphate,

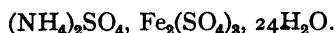
$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

From the weight of sodium pyrophosphate obtained, calculate the percentage of anhydrous disodium hydrogen phosphate in the original crystals.

Determination of the Iron in Ammonium Iron Alum

OUTLINE OF METHOD.—The salt is converted into ferric oxide by heating a crucible, and the percentage of iron in the alum is calculated from the weight of the oxide obtained.

This method of determining iron is applicable only to compounds that leave a residue, after ignition, consisting of pure ferric oxide. It cannot be used, therefore, for salts that contain a non-volatile impurity.

Procedure.—Weigh accurately in a tared crucible about 1·5 gram of ammonium iron alum,

$$(NH_4)_2SO_4,\ Fe_2(SO_4)_3,\ 24H_2O.$$

Heat the covered crucible and contents very gently over a small flame; gradually increase the temperature until full redness is attained, and then continue the ignition with a Méker burner for fifteen minutes. Cool for one minute, transfer to the desiccator for twenty to thirty minutes, and weigh. Repeat the ignition and weighing until the weight is constant.

The result of the experiment should be recorded as follows:—

Weight of crucible and alum	10·6842
Tare of crucible and lid	9·1722
Weight of alum taken	1·5120
Weight of crucible and Fe_2O_3 (1st ignition) .	9·4241
" " " (2nd ") .	9·4234
" " " (3rd ") .	9·4234
Weight of Fe_2O_3 obtained	0·2512

159·7 grams Fe_2O_3 represents 111·7 grams Fe, and the percentage of iron in the alum is therefore

$$\frac{0{\cdot}2512 \times 111{\cdot}7 \times 100}{159{\cdot}7 \times 1{\cdot}5120} = 11{\cdot}61$$

Percentage of iron required by the formula = 11·58
Difference = +0·03

The error is 3 in 1158, or +0·26 per cent. This corresponds to 0·6 mgrm. of ferric oxide.

Other Examples of Analysis by Ignition

Many other determinations may be carried out in the manner described in the last exercise. The method is easier and more expeditious than a precipitation method, but it is applicable only if the residue left after ignition is a pure substance, such as a pure oxide.

The residue left on ignition is usually an oxide. Before proceeding to the analysis, study the properties of the oxide

in order to ascertain to what extent it may safely be heated; as a rule, this information may be obtained by reference to Part V. of this book.

The following are typical cases in which this method may be used:—

Barium in barium peroxide and nitrate. The residue left after ignition is barium oxide, BaO.

Bismuth in bismuth oxynitrate and carbonate. The residue left after ignition is bismuth oxide, Bi_2O_3.

Calcium in calcium acetate, hydroxide, carbonate, and nitrate. The residue left after ignition is calcium oxide, CaO.

Copper in copper hydroxide, carbonate, and nitrate. The residue left after ignition is cupric oxide, CuO.

Lead in lead hydroxide, peroxide, carbonate, and nitrate. The residue left after ignition is lead monoxide, PbO.

Zinc in basic carbonate. The residue left after ignition is zinc oxide, ZnO.

It is often possible, by slight modification of the procedure, to apply this method to other salts, *e.g.*—

(1) The iron in ferrous ammonium sulphate may be determined by oxidation of a weighed sample with concentrated nitric acid and subsequent ignition. The residue obtained is ferric oxide.

(2) Some sulphates are completely converted into oxides by repeated ignition, with addition of a few small pieces of solid ammonium carbonate before each ignition.

Determination of Iron as Ferric Oxide

OUTLINE OF METHOD.—The iron, after oxidation to the ferric state if this should be necessary, is precipitated as ferric hydroxide by adding ammonia. The precipitate is filtered and washed. The filter is incinerated together with the precipitate, and the latter is converted into ferric oxide and weighed as Fe_2O_3.

Ferric Hydroxide is a reddish-brown, flocculent precipitate, practically insoluble in water, in dilute alkalis, and in ammonium salts, but readily soluble in acids. In order to obtain it free from basic salt, it should be precipitated by adding a moderate *excess* of ammonia to a cold or warm (but not boiling) solution,

the latter being continuously stirred. If washed free from the last trace of soluble salts, ferric hydroxide occasionally passes through the filter in the form of a brown colloidal solution. This can be prevented by washing the precipitate with a 2 per cent. solution of ammonium nitrate (*not* chloride) instead of with water.

Ferric Oxide, obtained by heating the hydroxide, is reddish-brown or almost black in colour, according to the temperature of the ignition. Contact with a reducing flame converts it partially into Fe_3O_4, or even into metallic iron. It is inadvisable to ignite at a higher temperature than can be obtained by a Bunsen burner, as Fe_3O_4 may be formed even in absence of reducing gases. If ferric oxide is ignited with ammonium chloride, ferric chloride volatilises. The ignited oxide dissolves very slowly in concentrated hydrochloric acid.

Exercise.—Weigh accurately, in a scoop or watch-glass, about 1·3 gram of ammonium ferric sulphate $(NH_4)_2SO_4, Fe_2(SO_4)_3, 24H_2O$ (ammonium iron alum). Transfer it to a 400 ml. resistance-glass beaker, provided with a suitable clock-glass and stirring-rod (see Fig. 8, p. 27). Dissolve the salt in water, add 5 ml. of dilute sulphuric acid, and determine the iron as follows.

Procedure.—Dilute to about 150 ml., warm the solution and precipitate the iron as ferric hydroxide by adding a moderate excess of dilute ammonia (15 to 20 ml.), the solution meanwhile being continuously stirred. For very accurate work, the ammonia should be freshly prepared by solution of the gas. Leave the stirring-rod in the beaker, cover the beaker with the clock-glass, and heat the contents until boiling. Boil for about one minute, and make sure that ammonia is present in the escaping steam. Remove the flame, place the beaker on a paper mat, rinse the underside of the clock-glass into the beaker with hot water, and allow the precipitate to settle.

Before commencing to filter the precipitate, read the general instructions regarding the filtration and washing of precipitates given on pp. 31 to 36.

Fit a 7-cm. funnel with an 11-cm. paper. For this precipitate, the type of funnel shown in Fig. 19 on p. 37 and the open-texture variety of filter paper (p. 32, footnote) are preferable.

Begin the filtration by decanting as much as possible of the clear liquid into the filter without disturbing the precipitate ;

pour the liquid down the stirring-rod, the latter being held against the rim of the beaker, and direct the liquid against the side of the filter and not into the apex (Fig. 15, p. 31). Do not fill the filter paper quite to the brim. Replace the beaker on the paper mat, add about 80 ml. of hot water—pour the water against the side of the beaker in order to avoid loss by splashing—and stir well. Allow the precipitate to settle, and once more decant the clear liquid into the filter. Repeat this process three times.

Now transfer the precipitate to the filter by pouring as much of it as possible into the latter, and, by means of a jet of hot water, washing the remainder into the filter in the manner described on p. 35. Remove any traces of precipitate adhering to the beaker and stirring-rod by rubbing with another stirring-rod tipped with rubber tubing.

Any precipitate that cannot be removed in this way must be dissolved in dilute nitric acid (2 to 3 drops mixed with 1 ml. of hot water), which is brought into contact with the entire surface of the beaker by means of the stirring-rod; a few drops of ammonia are then added in order to reprecipitate the ferric hydroxide, and the minute precipitate is collected in a separate *small* filter which is then carefully washed.

Finally, carefully scrutinise the beaker in a good light in order to make sure that no trace of precipitate remains. A small piece of moistened filter paper should be rubbed round the inside of the beaker, and if any stain is visible on this, the paper should be added to the precipitate.

The precipitate and filter paper must now be thoroughly washed in the following manner:—(1) Direct a fine stream of hot water against the filter paper—blowing gently at first in order that the impact of the water-jet will not cause a portion of the precipitate to be projected out of the funnel—and then, with a rotary motion of the wash-bottle jet, wash the precipitate as far as possible into the lower part of the filter. Allow the filter to drain completely, and repeat. (2) Direct the water-jet round the margin of the filter paper—which must be washed with great care—and then into the mass of the precipitate, which should be well churned up in the operation. Allow to drain, and repeat the washing until the filtrate is found to be free from sulphate, using for the later stages a hot 2 per cent. solution of ammonium nitrate in order to prevent the formation

of a sol of ferric hydroxide which would pass through the filter. In order to test for sulphate, rinse the end of the funnel-stem with water, and then collect about 1 ml. of the filtrate in a test-tube; add a few drops of barium chloride solution, and warm. When no turbidity is observed, the washing is complete.

While the filtration is in progress, a clean crucible (porcelain or platinum) is ignited at a red heat, cooled in a desiccator for thirty minutes, and weighed. The filter, together with the precipitate, is then incinerated without previous drying, in the manner described on p. 218. When the incineration is complete, ignite the ferric oxide with a full Bunsen flame in the partially covered crucible for ten minutes, cool in a desiccator for thirty minutes, and weigh. Repeat the ignition until constant weight is attained.

From the weight of Fe_2O_3 obtained, calculate the percentage of iron in ammonium iron alum.

The following example shows how the weighings should be recorded, the result calculated, and the error stated :—

Weight of scoop + iron alum	6·8244
Weight of scoop	5·4474
Weight of iron alum	1·3770
Weight of crucible	15·2816
Weight of crucible + Fe_2O_3 (1st ignition) .	15·5107
,, ,, ,, (2nd ,,) .	15·5102
,, ,, ,, (3rd ,,) .	15·5103
Weight of Fe_2O_3	0·2287

$$159{\cdot}7 \text{ grams } Fe_2O_3 = 111{\cdot}7 \text{ grams Fe.}$$

$$0{\cdot}2287 \text{ gram } Fe_2O_3 = 0{\cdot}2287 \times \frac{111{\cdot}7}{159{\cdot}7} \text{ gram Fe.}$$

$$\text{Percentage of iron found} = 0{\cdot}2287 \times \frac{111{\cdot}7}{159{\cdot}7} \times \frac{100}{1{\cdot}377} = 11{\cdot}61$$

Percentage of iron calculated from the formula of iron alum . . . . = 11·58
Difference . . . = + 0·03
Error (3 in 1158) . . = + 0·26 per cent.
= + 0·6 mgrm. of Fe_2O_3.

Determination of Aluminium as Oxide

OUTLINE OF METHOD.—The aluminium is precipitated as aluminium hydroxide by means of ammonia in presence of ammonium chloride. The precipitate is converted into the oxide by ignition, and is weighed as Al_2O_3.

Aluminium Hydroxide is a bulky, gelatinous precipitate, slightly soluble in ammonia, but almost insoluble in ammonia containing ammonium salts. Freshly precipitated aluminium hydroxide dissolves readily in dilute acids, but after keeping for some time it becomes almost insoluble. It is converted into alumina by ignition ; a very high temperature is required for complete dehydration.

Aluminium Oxide (*Alumina*), obtained from the hydroxide by ignition, dissolves very slowly in hot concentrated hydrochloric acid. It may be brought into solution easily after fusion with potassium pyrosulphate. It is not decomposed or volatilised at the highest temperature attainable with a blowpipe flame.

Exercise.—Weigh accurately, in a scoop or a watch-glass, about 1·4 grams of ammonium aluminium sulphate, $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$. Transfer it to a 400 ml. beaker provided with a clock-glass cover and stirring-rod. Dissolve in water, and determine the aluminium as follows.

Procedure.—Dilute the solution to about 100 ml. and add 10 ml. of concentrated hydrochloric acid and 40 ml. of dilute ammonia, which, for accurate work, should be freshly prepared by solution of the gas. Heat until almost boiling, add 1 ml. of methyl red indicator followed by dilute ammonia, drop by drop, until the solution becomes distinctly yellow (avoid excess). Boil for two minutes. Filter, and wash the precipitate in the same manner as described for ferric hydroxide (p. 226), using a hot 2 per cent. solution of ammonium nitrate instead of hot water throughout.

Dry the precipitate (partially at least) in the steam-oven. Incinerate the filter in presence of the precipitate in a weighed platinum crucible (p. 218). Ignite with a full Bunsen flame for a few minutes, and then for ten minutes with a Méker burner or a blowpipe. Cool, and weigh. Repeat the ignition until constant weight is attained.

Calculate the percentage of aluminium in the ammonium aluminium sulphate. Record all weighings, and state the error of the result in the same way as shown on p. 228.

Determination of Chloride as Silver Chloride

OUTLINE OF METHOD.—The chloride is precipitated as silver chloride by the addition of silver nitrate. The precipitate is filtered in the usual way, and, after incinerating the filter, is weighed as AgCl; or, preferably, the precipitate is collected and weighed in a Gooch or sintered glass crucible.

Silver Chloride is not quite insoluble in water. At 18°, 1 litre of water dissolves 1·5 mgrm. It is much more soluble in hot water, 1 litre of which, at 100°, dissolves nearly 22 mgrms.; for this reason, a silver chloride precipitate must be washed with *cold water*. The solubility in very dilute hydrochloric and nitric acids and in dilute silver nitrate solution is very small; on the other hand, silver chloride is decidedly soluble in concentrated hydrochloric acid and in concentrated solutions of silver nitrate and most chlorides (1 litre of saturated sodium chloride solution dissolves 1 gram of silver chloride).

On exposure to sunlight, silver chloride loses chlorine, becoming first violet and then nearly black; and, although this change is at first superficial, the loss of weight is appreciable. Silver chloride melts at about 455° and volatilises appreciably.

Exercise.—Weigh accurately about 0·4 gram of barium chloride, $BaCl_2, 2H_2O$. Transfer it to a 300 ml. beaker, dissolve in water, and determine the chloride as follows.

Procedure.—Dilute the solution to about 100 ml., and add 5 ml. of dilute nitric acid. To the cold solution add silver nitrate solution gradually, while stirring briskly, until precipitation of the chloride is complete. A large excess of silver nitrate must not be added and is easily avoided, since the precipitate coagulates as soon as a small excess of silver nitrate is present. In order to protect the silver chloride from bright light, wrap a piece of brown paper round the beaker (use a rubber band to fix the paper in place). Place the beaker on the steam-bath, and stir the liquid frequently until the precipitate has completely coagulated and the liquid is perfectly clear. Make certain that precipitation is complete by adding another drop of silver nitrate, and then allow the solution to cool.

Decant the clear liquid through a 9-cm. filter, and wash the precipitate several times by decantation with cold water containing a few drops of nitric acid. (The nitric acid prevents the silver chloride becoming colloidal and passing through the filter.) Transfer the precipitate to the filter in the usual way, and wash with cold water acidified with nitric acid, until a portion of the filtrate gives no turbidity with dilute hydrochloric acid. Finally, wash with pure water until the filtrate is free from acid (test with litmus paper). Dry the precipitate in the steam-oven.

Incinerate the filter, apart from the precipitate, in a porcelain crucible in the manner described on p. 219. The carbon should be burned at as low a temperature as possible. By means of a glass rod, add 2 drops of concentrated nitric acid to the ash in the crucible and warm gently; then add 1 drop of concentrated hydrochloric acid and cautiously evaporate to dryness. (The object of this procedure is to convert into silver chloride the metallic silver produced during the incineration of the filter.) Transfer the precipitate to the crucible, and either heat the open crucible for five minutes with a very small flame, great care being taken not to fuse the precipitate, or dry the precipitate in the air-oven at 130° for an hour. Cool, and weigh.

A more convenient method of filtering silver chloride is by means of a Gooch crucible with an asbestos filter (p. 212), or a sintered glass crucible (p. 214). The crucible is dried in the air-oven at 150° and weighed. After collecting and washing the precipitate in the crucible the latter is heated for an hour in the oven at 130°, and is then cooled and weighed.

From the weight of silver chloride obtained, calculate the percentage of chloride in the barium chloride.

Determination of Copper as Cupric Oxide

OUTLINE OF METHOD.—The copper is precipitated as hydrated copper oxide by means of sodium hydroxide. The filter is incinerated apart from the precipitate, and the latter is converted into cupric oxide by ignition, and is weighed as CuO.

Copper Hydroxide, precipitated from a cold solution, is a light blue substance which becomes dark brown or black when boiled with the alkaline solution. The change in colour is due to loss of water, the composition of the black precipitate being

probably $3CuO, H_2O$. The precipitate is slightly soluble in sodium hydroxide solution, and readily soluble in ammonia and in dilute acids. Precipitation is incomplete in presence of organic matter or ammonium salts.

Cupric Oxide, produced from the hydrated oxide by ignition, is a black, hygroscopic powder, which remains unaltered at a red heat, provided reducing gases are carefully excluded.

Exercise.—Weigh accurately about 0·8 gram of copper sulphate, $CuSO_4, 5H_2O$. Transfer it to a 400 ml. Pyrex beaker or a large casserole, dissolve in water, and determine the copper as follows.

Procedure.—Dilute the solution to about 150 ml. and heat until almost boiling. Remove the flame, add 1 ml. of phenolphthalein, and drop in from a burette, while stirring, a dilute solution of pure sodium hydroxide until the supernatant liquid is definitely pink. A *large* excess of alkali must be carefully avoided. Boil the contents of the covered vessel for about one minute, and then allow the precipitate to subside.

Decant the clear liquid through a 9-cm. filter, and wash the precipitate several times with hot water by decantation. Transfer the precipitate to the filter. Wash the precipitate and the filter—especially the margin of the latter—until a portion of the filtrate gives no turbidity on boiling with 1 drop of dilute hydrochloric acid and 1 ml. of barium chloride solution.

It frequently happens that a small quantity of the copper oxide adheres to the side of the beaker and cannot be detached by rubbing with a rubber-tipped stirring-rod. In order to remove it, add 2 drops of dilute nitric acid, and bring the acid into contact with the entire surface of the beaker by means of the stirring-rod ; rinse down the interior of the beaker with a very little hot water, heat the solution to the boiling-point over a minute flame, and reprecipitate the copper oxide by adding a few drops of sodium hydroxide (avoid excess). Transfer the minute precipitate at once to a separate *small* filter, and wash thoroughly.

Dry both filters very thoroughly in the steam-oven. Incinerate the filters, the larger one apart from the precipitate, in a weighed porcelain crucible in the manner described on p. 219. When all the carbon is burned, allow the crucible to cool and moisten the ash with 2 drops of concentrated nitric acid in order to oxidise any reduced oxide formed during the

incineration. Heat the crucible very gently with a minute flame until fuming ceases, and then heat to dull redness for about a minute. When the crucible has become nearly cold again, place it on glazed paper, and carefully transfer the main precipitate to the crucible.

Heat the copper oxide in the open crucible to dull redness for five minutes, cool in a desiccator as usual, and weigh. Repeat the ignition until constant weight is attained. During the ignition every care must be taken that reducing gases are excluded from the interior of the crucible, and for this purpose a perforated silica plate or asbestos board (p. 211), instead of a pipe-clay triangle, should be used to support the crucible.

From the weight of the copper oxide obtained, calculate the percentage of copper in the copper sulphate.

Determination of Zinc as Oxide

OUTLINE OF METHOD.—The zinc is precipitated as basic carbonate by means of sodium carbonate. The filter is incinerated apart from the precipitate, and the latter is converted into zinc oxide by ignition, and is weighed as ZnO.

Basic Zinc Carbonate, the composition of which varies according to the conditions of precipitation, is a white powder, very slightly soluble in water, and readily soluble in acids, alkali hydroxides, and ammonia. It is slightly soluble in sodium carbonate, and excess of the reagent must therefore be avoided. If the zinc solution contains much sulphate, sodium carbonate always precipitates some basic sulphate, and the precipitate, after filtration, must be dissolved again and reprecipitated ; with a small amount of sulphate this is unnecessary. The basic carbonate is converted into zinc oxide by ignition.

Zinc Oxide is yellow when hot, but almost white when cold. It may be heated to bright redness without volatilisation ; but if carbonaceous matter, such as traces of filter paper, is present, partial reduction to metallic zinc occurs, and the zinc volatilises readily.

Exercise.—Weigh accurately about 0·8 gram of zinc sulphate, $ZnSO_4, 7H_2O$. Transfer it to a 300 ml. Pyrex beaker or casserole, dissolve in water, and determine the zinc as follows.

Procedure.—Dilute to about 100 ml., and to the cold solution add sodium carbonate (not ammonium carbonate) solution drop by drop until a faint turbidity appears; then heat until boiling. In this way the greater part of the zinc is precipitated as basic carbonate free from alkali carbonate. Now add 1 ml. of phenolphthalein and more sodium carbonate until the solution becomes distinctly pink. Boil for several minutes.

After the precipitate has settled, decant the clear liquid through a 9-cm. filter, and wash the precipitate three times with hot water by decantation. Transfer the precipitate to the filter, and continue the washing until a portion of the filtrate gives no turbidity with hydrochloric acid and barium chloride (p. 231).

Dry the precipitate and the filter in the steam-oven. Separate the precipitate as completely as possible from the filter, without, however, rubbing off any paper fluff, and wrap up the paper in the manner described on p. 220. In order to prevent as far as possible the reduction of any zinc oxide still adhering to the filter paper, moisten the paper with a few drops of ammonium nitrate solution, and dry it in the steam-oven for a few minutes. Incinerate the paper in a weighed porcelain crucible at as low a temperature as possible. When all the carbon is burned, add the precipitate, and heat the crucible gently at first, and then to bright redness for ten minutes. Use a good oxidising flame and take care to exclude flame gases during the ignition, otherwise reduction of the oxide and loss of zinc (by volatilisation) will occur. Cool, and weigh. Repeat the ignition until constant weight is attained.

From the weight of zinc oxide obtained, calculate the percentage of zinc in zinc sulphate.

Note.—In order to avoid the risk of loss during the incineration of the filter, the zinc carbonate may be filtered by means of a Gooch crucible (see p. 212). The crucible containing the precipitate is dried in the steam-oven or air-oven, and is then placed in a larger nickel crucible, or small tin on the bottom of which is a thin sheet of asbestos, and ignited with a full Bunsen flame.

Determination of Sulphate as Barium Sulphate

OUTLINE OF METHOD.—The sulphate is precipitated as barium sulphate by the addition of barium chloride, and the precipitate, after ignition, is weighed as $BaSO_4$.

Barium Sulphate, obtained by precipitation, is a fine, white powder which is not quite insoluble in water. At 18°, 1 litre of water dissolves 2·3 mgrms. It is from twenty to thirty times more soluble in cold dilute (normal) hydrochloric and nitric acids. It dissolves freely in concentrated sulphuric acid, but is reprecipitated on diluting the acid. In dilute sulphuric acid and in barium chloride solution it is practically insoluble. Barium sulphate may be ignited in air at a red heat without alteration of weight.

The marked tendency of barium sulphate to carry down traces of other substances contained in the solution is a common source of error in the determination of sulphate. The co-precipitated substances cannot always be removed by washing or ignition, and the results are accordingly high; sometimes loss of sulphuric acid occurs on ignition, and low results may be obtained. In order to reduce the error to a minimum, and to obtain a granular precipitate suitable for filtration, the following conditions must be observed :—

1. The solution must be free from iron (ferric), aluminium, chromium, nitrate, and chlorate. The metals can be removed by precipitation with ammonia; nitrate and chlorate by repeated evaporation with concentrated hydrochloric acid.

2. The solution should contain a little hydrochloric acid (about 2 per cent. by volume of the dilute acid), and its volume should not be less than 250 ml. for each 0·5 gram of barium sulphate.

3. The barium chloride solution should be dilute (about 3 per cent.), and may be acidified with a few drops of dilute hydrochloric acid.

4. Precipitation must take place slowly, the hot barium chloride solution being added drop by drop to the

nearly boiling sulphate solution, and an excess (about 5 ml.) of the barium chloride should be introduced after the precipitation is complete.[1]

Exercise.—Weigh accurately about 0·6 gram of magnesium sulphate, $MgSO_4$, $7H_2O$. Transfer it to a 400 ml. beaker, dissolve in water, and determine the sulphate as follows.

Procedure.—Dilute the solution to about 250 ml., add 5 ml. of dilute hydrochloric acid, and heat until boiling. Prepare an approximately 3 per cent. solution of barium chloride ($BaCl_2$, $2H_2O$), acidify about 30 ml. of the solution with a few drops of dilute hydrochloric acid, and heat until boiling. Lower the flame under the magnesium sulphate solution until the latter just ceases to boil, rinse the cover-glass into the beaker, and add the *hot* barium chloride solution drop by drop[2]; stir constantly while precipitation is in progress.

When the precipitation appears to be complete, allow the precipitate to settle, and ascertain whether the addition of a few more drops of barium chloride produces any further precipitate. If no turbidity appears immediately, make sure that there is none after waiting for a minute. (In order to avoid incomplete precipitation, particular care is necessary at this stage, since the precipitation of barium sulphate from a dilute solution is not visible immediately the reagent is added.) After all the sulphate is precipitated, add an additional 5 ml. of barium chloride solution, stir briskly, and then set the beaker aside for about an hour.

Decant the clear liquid through a 9-cm. filter, and wash the precipitate twice with hot water (by decantation). Transfer the precipitate to the filter. Wash the precipitate and the filter with hot water, until a portion of the filtrate gives no turbidity with a few drops of silver nitrate.

[1] If the barium chloride is added rapidly, the precipitate will contain an appreciable amount of chloride. After precipitation is complete, however, an excess of barium chloride may safely be added, in order to diminish the solubility of the barium sulphate.

[2] A simple form of dropping-tube, by means of which the barium chloride (or other reagent) can be added slowly, is made by drawing out a test-tube in the blowpipe flame so as to form a capillary through which the solution will pass at the rate of about 2 drops per second. The tube, charged with the hot barium chloride solution, is supported over the beaker in a clean clamp. A funnel attached by rubber tubing to a glass tube drawn out to a capillary may be used instead.

Incinerate the filter in a weighed crucible in the manner described on p. 218 after drying. After all the carbon is burned, allow the crucible to cool. In order to convert into sulphate any sulphide that may have been formed during the burning of the filter paper, add 2 or 3 drops of a mixture consisting of 1 ml. of alcohol and 2 drops of concentrated sulphuric acid. Warm very gently until the excess of sulphuric acid has volatilised, and then ignite with a full Bunsen flame for ten minutes. Cool, and weigh. Repeat the ignition until constant weight is attained.

The filtration, drying, and weighing may more conveniently be carried out in a Gooch or sintered glass crucible, as described under the determination of chloride (p. 231).

From the weight of barium sulphate obtained, calculate the percentage of sulphate (SO_4) in the magnesium sulphate.

Determination of Calcium as Oxalate

OUTLINE OF METHOD.—The calcium is precipitated as calcium oxalate by means of ammonium oxalate, and the precipitate is either weighed as the monohydrate, or, after conversion into calcium oxide or calcium sulphate, is weighed as CaO or $CaSO_4$.

Calcium Oxalate, CaC_2O_4, H_2O, is a fine, white powder which is very slightly soluble in water. At 18°, 1 litre of water dissolves about 6 mgrms. It is more soluble in hot water; at 95°, 1 litre of water dissolves about 14 mgrms. In dilute ammonia it is somewhat less soluble than in water. It dissolves easily in hydrochloric and nitric acids, but very sparingly in acetic acid. It is somewhat soluble in magnesium chloride solution. Dried at 100°, the precipitate has the composition of the monohydrate; if heated to a temperature approaching dull redness, it is converted into calcium carbonate.

Calcium Carbonate may be heated to about 500° without appreciable decomposition. The dissociation pressure increases (slowly at first and then rapidly) with the temperature, and if heated above 800° in a vessel from which the carbon dioxide can escape, it is completely converted into calcium oxide.

Calcium Oxide is a hygroscopic substance, and should be exposed to the air as little as possible during weighing. As it also absorbs carbon dioxide readily, it should be kept in a desiccator containing soda-lime or sticks of sodium hydroxide.

Calcium Sulphate remains unaltered at a dull red heat. Slow decomposition, with loss of sulphur trioxide, occurs at bright redness.

Exercise.—Weigh accurately 0·4 to 0·5 gram of powdered calcite (calcspar). Transfer it to a 400 ml. beaker. Add about 10 ml. of water, cover the beaker with a clock-glass, and dissolve the calcite by adding dilute hydrochloric acid (about 10 ml.). Dilute with a little water, and boil the solution for a few minutes in order to free it from carbon dioxide. Determine the calcium as follows.

Procedure.—Add a few drops of methyl orange, and carefully neutralise the solution with ammonia. Then add 1 ml. of dilute hydrochloric acid, dilute the solution to about 200 ml., heat until boiling, and add a moderate excess (25 to 30 ml.) of a boiling 2 per cent. solution of ammonium oxalate (freshly prepared). Then slowly make the mixture alkaline with ammonia, and boil for a few minutes, care being taken, by stirring, to avoid bumping. Set the beaker aside for one hour.

Filter through a 9-cm. paper, and wash the precipitate three times by decantation with cold, dilute ammonia (25 ml. of 2N ammonia diluted to 100 ml.). Transfer the precipitate to the filter, and continue the washing, preferably with a saturated solution of calcium oxalate until a portion of the filtrate gives no turbidity with nitric acid and silver nitrate.

(1) *If the precipitate is to be weighed as the monohydrate of calcium oxalate,* it must be filtered in a Gooch or sintered glass crucible, and washed as described above. Finally, it is washed either with three small portions of alcohol followed by similar treatment with ether, or with five small portions of acetone. In either case the crucible is then placed in an oven at 80° to 100° for half an hour, cooled, and weighed.

(2) *If the precipitate is to be converted into and weighed as calcium oxide,* incinerate the filter, together with the still moist precipitate, in a weighed *platinum* crucible, in the manner described on p. 218. After all the carbon is burned, heat the crucible, gently at first, and then with a Méker burner for twenty minutes. Cool, and weigh. Repeat the ignition (for ten minutes) until constant weight is attained.

(3) *If the precipitate is to be weighed as calcium sulphate,* a porcelain or silica crucible may be used. Proceed as in (2), but ignite with a Méker burner for five minutes only. Cool,

and then slake the calcium oxide by pouring about 1 ml. of water into the crucible. (The water must be added all at once, not drop by drop.) Then add an excess (about 10 drops) of concentrated sulphuric acid. Heat the crucible in an air-bath (Fig. 42, p. 213), gently at first and then with a full Bunsen flame, until the excess of sulphuric acid has been volatilised. Ignite the dry sulphate at low redness, cool, and weigh. Repeat the treatment with acid (add a few drops only), etc., until constant weight is attained.

Electrolytic Methods

ELECTROLYTIC methods are confined almost entirely to the determination of metallic radicals and, as a rule, the metal is deposited as such on the cathode. In the case of lead, it is found better so to adjust the conditions of electrolysis that the lead is deposited as lead dioxide on the anode. If a metal is to be determined electrolytically, it must (1) be deposited in a pure state; (2) be deposited completely from the solution; and (3) form a coherent deposit on the electrode.

The nature of the deposit and the accuracy of the determination depend on a number of conditions, among which are the rate of deposition, the composition of the solution, and the temperature. The correct conditions vary for different metals and must be adjusted for each metal within fairly narrow limits. Important factors are potential difference, current density, temperature, hydrion concentration, and composition of the electrolyte. Current density is the amount of current, measured in amperes, per 100 sq. cm. of cathode surface immersed in the solution. Thus, if a current of 1·5 ampere is used and the area of cathode immersed is 75 sq. cm., the current density is $1{\cdot}5 \div 0{\cdot}75 = 2$.

For occasional analyses in which speed is not essential, stationary electrodes may be employed. A platinum dish, crucible, or stout wire can be used as the cathode, if specially designed electrodes are not available. For routine analyses, where speed is essential, it is necessary to use a rotating electrode in order to keep that portion of the electrolyte which is in close proximity to the electrodes in rapid circulation. Otherwise the high current density which is of necessity being used causes liberation of hydrogen on the cathode, preventing the deposited metal from adhering satisfactorily. The conditions for rapid movement of the electrolyte are attained by the use of electrodes such as those designed by Sand (see p. 243).

To obtain the high current density required to effect a reasonably rapid deposition, the resistance of the electrolyte must be kept as low as possible. The type of Sand's electrodes which consists of two concentric wire gauze cylinders satisfies this condition, since the distance between them is only of the order of 3 millimetres.

Separations.—It is often possible to separate metals and estimate them quantitatively by electrolytic means, making use of the difference between their deposition potentials. As an illustration of this the estimation of copper and nickel in a mixture of their sulphates may be cited. To the solution a potential difference of not more than 2 volts is applied, and the current noted. So long as any copper remains, the voltage at the electrodes will vary but little, and no nickel will be deposited. After all the copper has been removed, however, a sharp rise in the voltage will be required to maintain the current density. The cathode may now be weighed to determine the copper, and the nickel then deposited, using a higher voltage.

A more satisfactory method depends on the result of altering the hydrion concentration of the electrolyte considerably between the deposition of the two metals. An example of this method is given on p. 248.

Composition of the Solution.—Sulphates and nitrates are often the best electrolytes, but it is sometimes necessary to use solutions containing complex salts, such as " double " oxalates, tartrates, or cyanides, in order to obtain satisfactory and complete deposition of the metal. The concentration of acid present is often an important condition, especially in securing the separation of metals. The presence of hydrochloric acid, or of a chloride in an acid solution must be avoided, since the chlorine discharged at the anode will attack the platinum. If chloride is present, it should be expelled by evaporating the solution with concentrated sulphuric acid.

Source of Current.—By far the most satisfactory source of current for this work is a battery of lead accumulators capable of giving up to 5 amperes at an E.M.F. of 2 to 10 volts. The specific gravity of the acid must be tested from time to time. It is not advisable to run an accumulator after the voltage has fallen below 1·9 volt, or the specific gravity below about 1·1.

Stationary Electrodes.—For some purposes, a platinum

basin holding about 150 ml. of liquid is a convenient cathode. The inner surface should be roughened (suitable basins with the surface roughened by a sand-blast may be purchased) in order that the deposit may adhere firmly. This roughened surface must never be cleaned with sand or other abrasive material. As anode, a stout perforated platinum disc, shaped like a saucer (Fig. 52), may be used, or a stout platinum wire may be wound in a flat spiral as shown in Fig. 53. The stout platinum wire D is used to clamp the electrode in position and to make the electrical connection.

It is sometimes inconvenient to use a platinum basin to contain the electrolyte and to serve as cathode, *e.g.* in case it is necessary to remove the electrolyte and wash the deposit without interrupting the current (see p. 244). Instead of the basin electrode, the cathode may take the form of a cylinder of platinum gauze which is suspended, together with the anode, in a beaker containing the electrolyte. When the deposition is complete it is easy, with this arrangement, to remove the cathode and simultaneously to rinse it with water—without previously interrupting the current; or, instead, the beaker containing the electrolyte may be removed and another beaker, containing water, immediately substituted.

FIG. 52. FIG. 53.

A stand with insulation between the positive and negative terminals is convenient for use with a basin electrode, the basin being supported on a conducting plate; if a special stand is not available, the necessary insulation may be obtained by clamping the anode support D in a rubber cork, and fitting a terminal to the upper end.

Rotating Electrodes.—Rotating electrodes for use in rapid determinations have been designed by Sand. In one form, the cathode (Fig. 54), consists of a stationary platinum wire gauze cylinder attached by stout platinum wires to a split collar at the top. A glass tube with an expanded upper end slides tightly through this collar, and separates the two electrodes. The anode (Fig. 55) consists of a platinum wire gauze

cylinder of smaller diameter than the cathode, and is attached to a platinum-iridium tube of such a diameter that it will just fit inside the glass tube, but rotate freely within it. When the apparatus is set up, there is a clearance of only some 3 mm. between the inner and outer cylinders, so that the resistance of the electrolyte between them is very low. In another form

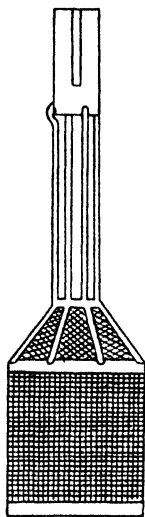
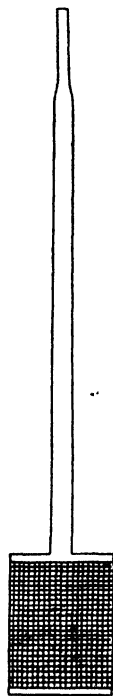
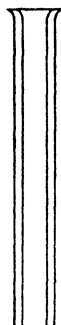



FIG. 54. FIG. 55.

the rotating anode has inside it a platinum partition designed to stir the liquid more effectively.

The platinum-iridium tube of the anode is gripped by a small chuck attached to a vertical spindle or shaft supported by a suitable bearing, and carrying a pulley at the top. Power from an electric motor is supplied to the pulley by belt drive, electrical contact with the rotating anode being made through the bearing, or, better, by means of a cup containing mercury at the top of the pulley. This latter method is essential if voltage measurements are to be made. Connection with the

cathode is made by a suitable clamp with a platinum-foil lining to prevent abrasion.

Sand (*Analyst*, 1929, vol. 54, p. 275) has later designed electrodes which require much less platinum for their construction. They consist of quartz glass frames on which is supported platinum wire gauze. The weight of platinum required is about 7 grams for the outer, and 4 grams for the inner electrode.

Siphon.—When the deposition is complete, it is often necessary to remove the electrolyte without stopping the current, otherwise partial re-solution of the deposit would occur. This is most easily accomplished in the case of a basin electrode by means of a siphon arranged as shown in Fig. 56. The short limb of the siphon should reach to the bottom of the basin, and to prevent abrasion it should be covered with a short piece of rubber tubing. The longer limb should be fitted with a rubber tube and spring-clip by means of which the rate of outflow may be regulated. To start the siphon, fill it with water, place it in position, and open the clip. Run water into the basin from a tap-funnel to replace the solution withdrawn. The water must be allowed to flow gently onto the surface of the solution, so that there is as little mixing as possible. When about 200 ml. of water has been used, stop the current, disconnect the apparatus, and complete the washing in the usual manner with the wash-bottle.

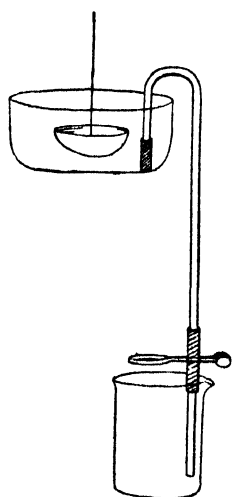



FIG. 56.

Measurement of Current.—An ammeter reading up to 5 or 6 amperes (not necessarily very accurately) and a high-resistance voltmeter recording up to 10 volts are required.

Regulation of Current.—It is necessary to have some form of adjustable resistance, such as a rheostat with a sliding contact, in the circuit. A rheostat with a maximum resistance of 20 ohms will be found suitable for most purposes.

Arrangement of Apparatus.—The positive pole of the battery is connected to the anode, and the negative pole to

the cathode, a rheostat and ammeter being inserted in series. If measurements of difference of potential in the electrolytic cell are required, the voltmeter is connected across the electrodes (Fig. 57).

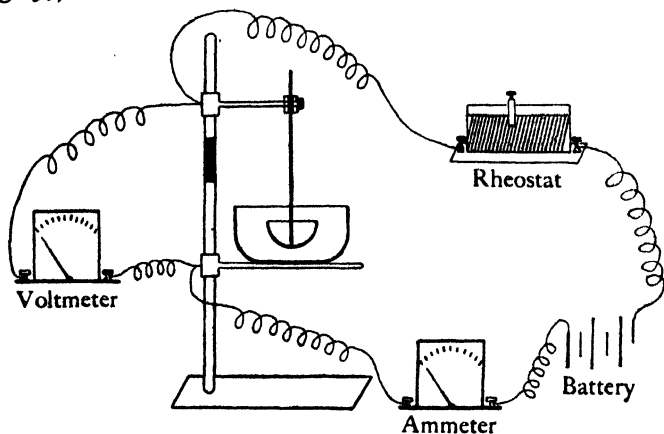



FIG. 57.—General Arrangement of the Apparatus.

Electrolytic Determination of Copper

(With Stationary Electrodes)

Copper is readily deposited from a copper sulphate solution by electrolysis, and forms a coherent deposit if the potential used is not above 2·2 volts. Further, the copper under these conditions is deposited in a pure state, even when the solution contains iron, nickel, and other metals. The time required for complete deposition is greatly increased when iron is present in the solution, but the precipitation is almost quantitative, even in presence of 1 gram of iron, if sufficient time is allowed. Nitrate and chloride interfere with this method, and if these radicals are present the solution must be evaporated with 2 to 3 ml. of concentrated sulphuric acid until complete conversion into sulphate is effected, and dense white fumes are evolved.

Procedure.—Clean the platinum basin with sodium hydroxide in order to remove grease, then with nitric acid, and finally with water. Drain the basin—but do not touch the interior with the fingers or wipe it with a cloth—place it in the steam-oven for half an hour, cool, and weigh.

Weigh out accurately about 1·3 gram of copper sulphate, dissolve in water in the tared platinum basin, dilute the solution to 100 ml., and add about 5 ml. of dilute sulphuric acid. Use as an anode a sheet of platinum or a stout platinum wire. Cover the basin with a clock-glass cut into two pieces and provided with a notch for the anode wire. Connect the electrodes with an accumulator, without any intermediate resistance, and allow the current to pass for about twelve hours. It is often convenient to start the experiment late in the day and allow the current to pass all night.

Next morning, rinse the drops on the underside of the clock-glass into the basin and allow the electrolysis to continue for another hour. Switch off the current, remove the anode and rinse it quickly, and immediately pour the solution into a beaker. Without delay, rinse the basin several times with water, and then twice with alcohol (reject the alcohol washings). Dry the basin in the steam-oven for not more than ten minutes, then cool, and weigh.

Remove the deposit from the basin by means of hot, dilute nitric acid, and weigh the clean, dry basin again. Pour back the solution and pass the current again for an hour, and reweigh. (Any further deposit of copper will be readily seen on the clean surface of the platinum.) If the weight is unchanged, it may be assumed that all the copper is deposited.

Electrolytic Determination of Copper

(With a Rotating Electrode)

The main object of employing a rotating electrode for this determination is to bring about a continuous movement of the electrolyte at its surface, thus preventing local depletion of copper ions, with the resulting evolution of hydrogen, at current densities sufficiently high for rapid electrolysis. A further advantage lies in the fact that the deposition of copper may be carried out in a solution containing nitric acid, which is used in dissolving copper alloys and ores, as with a rotating electrode any local concentration of nitrous acid formed by reduction is prevented. The previous removal of nitrate by evaporation with sulphuric acid may therefore be dispensed with.

The following method for the determination of copper is convenient and accurate, and it may be used to separate copper

from cobalt, nickel, zinc, and iron. The solution must contain about 3 per cent. of nitric acid. It must be free from chloride and from more than a trace of nitrite, both of which may be removed, if necessary, by evaporation with sulphuric acid (p. 365).

The main difficulty in this method is to prevent re-solution of copper during the washing process; this is due to the presence of *nitrous* acid, formed by electrolytic reduction of the nitric acid. If the nitrous acid is destroyed by adding a little hydrogen peroxide or urea, just before interrupting the current, no copper is redissolved by the nitric acid.

Procedure.—A suitable amount of copper for deposition is about 0·25 gram. If it is in the metallic form, it is dissolved in a 150 to 200 ml. narrow beaker, in 10 ml. of concentrated nitric acid diluted with 10 ml. of water. The solution is boiled to expel oxides of nitrogen. The free acid is neutralised with ammonia, 3 ml. of concentrated nitric acid are added, and the solution diluted to about 100 ml. To destroy any nitrous acid that may still be present, add half a gram of urea and warm. If the copper is already in solution, any free acid is neutralised with ammonia, and 3 ml. of concentrated nitric acid are added. The solution is then diluted to about 100 ml.

The cathode is cleaned in hot dilute sodium hydroxide followed by dilute nitric acid, rinsed with water and finally with industrial alcohol. It is dried in a steam-oven and weighed. The electrodes are fitted up, and connected in a circuit as described on p. 244, four lead accumulators being used. The motor driving the rotating chuck is started, to see that the adjustment of the electrodes is correct. The beaker containing the copper solution is now raised until the cathode is almost completely immersed. It is covered by the two halves of a watch-glass, through the centre of which, before splitting, a suitable hole has been bored. The motor is restarted and allowed to run at such a speed that the anode is rotating at about 800 revs. per min. The current is now switched on, and adjusted to about 0·5 ampere until a layer of copper has been deposited on the cathode, when the current is raised to 3 amperes. The progress of the electrolysis can be gauged from the colour of the solution. When the solution is colourless, rinse the undersides of the watch-glass into the beaker, and after a few minutes test 1 ml. of the solution with sodium

acetate solution and sulphuretted hydrogen to ensure that all the copper has been deposited. Add 1 gram of urea, and after a minute reduce the current to half an ampere. Remove the beaker and rapidly replace it with one containing distilled water. Stop the motor, cut off the current, disconnect the electrodes, and wash the cathode with alcohol. Dry in a steam-oven, and weigh.

Electrolytic Determination of Nickel

If copper is present in the original solution, it must be removed by deposition from an acid solution, as already described. If nitrate is present, it must be removed by evaporation with concentrated sulphuric acid (p. 365). Chloride and sulphate do not interfere with the process.

Procedure.—The amount of substance taken should preferably be such as will yield about 0·3 gram of nickel. Make the solution approximately neutral, add 5 grams of ammonium sulphate and 20 ml. of concentrated ammonia, and dilute to about 120 ml.

The arrangement of the apparatus should be exactly as described above for the determination of copper with a rotating cathode, except that the beaker containing the solution must be supported above a wire gauze.

By means of a small flame, raise the temperature of the solution to 60°-80°, and keep it between these limits during the electrolysis. Use three or four accumulator cells, and adjust the initial current to about 0·5 ampere. Increase the current gradually to about 3 amperes. When the solution is colourless, rinse the watch-glass into the beaker, and after a further five minutes test for nickel in 1 ml. of the solution by the addition of hydrogen sulphide.

When all the nickel is deposited, reduce the current to about 0·5 ampere and rapidly replace the beaker by one containing distilled water. Stop the motor, switch off the current, and finish the determination as in the case of copper above.

Exercise.—Determine the percentages of copper and nickel in a sample of "Constantan" wire, or "Monel" metal. Dissolve a weighed portion (about 0·5 gram) in 10 ml. of concentrated nitric acid mixed with an equal volume of water. Boil the solution for a few minutes, neutralise with ammonia,

add 2 to 3 ml. of concentrated nitric acid and 0·5 gram of urea, and dilute to 100 ml. Deposit and weigh the copper as described above. The water used for washing the electrodes is added to the electrolysed solution, and the whole evaporated with sulphuric acid to remove nitrate (see p. 365). Dilute, and determine the nickel as described above, omitting the addition of ammonium sulphate.

Electrolytic Determination of Cadmium

Cadmium is readily deposited electrolytically from solutions of most cadmium salts, but in order to obtain a pure coherent deposit it is best to use a solution of potassium cadmium cyanide.

Procedure.—To the cadmium solution, containing 0·3 gram of cadmium, add 1 ml. of phenolphthalein solution, and then pure 2N sodium hydroxide solution until a pink coloration is produced; then add a further 2 to 3 ml. While stirring the solution, add slowly a 5 per cent. solution of potassium cyanide until the precipitate produced at first is redissolved. An additional 10 ml. is then added.

Dilute to 100 ml., and electrolyse the solution, using a rotating anode, at 70°. It is advisable, though not essential, to deposit a layer of copper upon the cathode before the cadmium. The electrolysis and washing are carried out as described for copper (p. 247), except that the initial current should not exceed 0·2 ampere. The current is later raised to 3 amperes, and after three-quarters of an hour 1 ml. of the solution is tested for cadmium by boiling with dilute hydrochloric acid to remove cyanide (CARE!), and after dilution passing sulphuretted hydrogen. The cathode is dried and weighed in the usual manner.

Electrolytic Determination of Zinc

The most satisfactory electrolyte for the deposition of zinc is an alkaline zincate solution, containing excess of alkali. If a nitrate is present, it must be removed by evaporation with sulphuric acid (see p. 365). Ammonium salts, if present, must be decomposed by addition of excess of potassium hydroxide and boiling.

Zinc must not be deposited directly on platinum, and if a platinum cathode is to be used, this must be first covered with a layer of copper by electrolysis in copper sulphate, and the electrode washed, dried, and weighed.

Procedure.—To a solution of zinc sulphate containing 0·3 to 0·4 gram of zinc, add sodium hydroxide solution to neutralise any free acid, and then 8 to 10 grams of solid sodium hydroxide. Dilute the solution to about 100 ml., and using a rotating anode begin the electrolysis with a current of 0·5 ampere. After five or ten minutes raise the temperature to 60°, and increase the current to 2 amperes. When the electrolysis has proceeded for three-quarters of an hour, test 1 ml. of the solution with sodium sulphide to ascertain whether the deposition is complete. As the deposited zinc is liable to oxidise rapidly in air when wet, the electrolyte is best replaced by means of a siphon (see p. 244). Drying must be carried out at as low a temperature as possible, and washing with ether after alcohol is to be recommended for this reason.

Electrolytic Determination of Lead

Lead is always deposited as lead dioxide on the anode, and to prevent any separation of metallic lead on the cathode, a high concentration of nitric acid must be used. In the presence of a considerable amount of copper, however, a lower concentration of nitric acid is permissible as the deposition potential of metallic lead is not likely to be reached. Manganese interferes with the estimation of lead by this method and certain other metals may possibly contaminate the deposit, rendering it advisable in the presence of much impurity to dissolve and redeposit the lead dioxide. Chlorides must be absent.

Procedure.—To a solution of lead nitrate, containing about 0·3 gram of lead, add 15 to 20 ml. of concentrated nitric acid, and dilute to 85 to 100 ml. Before assembling the electrodes, clean the anode, dry at about 200° in an air-oven, and weigh. Heat the electrolyte to 50°, and adjust the current to about 3 amperes. After forty-five minutes, test 1 ml. of the liquid with sodium sulphide after neutralising. When the electrolysis is finished, stop the motor, and displace the electrolyte by distilled water, using a siphon as described on p. 244. Continue washing until the liquid is almost free from acid, stop the

current, and disconnect the anode. Rinse with distilled water, and dry as above. Even at 200° a trace of water is retained by the lead dioxide, making the result about 0·25 per cent. too high.

To remove the lead dioxide from the anode, place this in warm moderately concentrated nitric acid, containing a little glucose or oxalic acid.

Electrolysis with Stationary Electrodes

If preferred, the above electrolyses may be carried out with stationary electrodes. Smaller current densities must be used, and the duration of the electrolysis greatly increased. For a general outline, see the determination of copper with stationary electrodes (p. 245).

Electrolytic Analysis of Brass

OUTLINE OF METHOD.—The *copper* and *lead* are deposited simultaneously on the cathode and anode respectively. The *iron* is precipitated with ammonia, and weighed as ferric oxide. The *zinc* is then deposited on the cathode from alkaline solution. The *tin* is determined in a separate portion as metastannic acid.

Procedure.—Dissolve not more than 1 gram of the alloy in a mixture of 5 ml. of concentrated nitric acid and 10 ml. of about 60 the beaker to be used for the electrolysis. Dilute to water in ml., and boil for a few minutes to remove oxides of nitrogen. If the solution is not clear, owing to the presence of metastannic acid, filter into another beaker of the same size, washing the filter and neglecting the residue. Whether filtration has been necessary or not, dilute the solution to about 80 ml., and add 5 ml. of concentrated nitric acid. Electrolyse with a rotating anode, both anode and cathode being of platinum gauze and weighed before the experiment. Heat to 60°, and carry out the electrolysis as described for the deposition of lead (p. 250). After thirty minutes, by which time most of the lead present in the alloy will be deposited as lead peroxide on the anode, cool, and dilute to 160 ml. Finish the electrolysis as described for the deposition of copper (p. 247). Wash and dry the electrodes, and weigh them as directed on pp. 248 and 250. Leave the copper deposit on the cathode.

Precipitate the iron from the solution, after the deposition of the copper and lead, by double precipitation with ammonia as described on p. 367, and weigh the iron as Fe_2O_3.

Evaporate the combined filtrate and washings from the iron precipitation to about 100 ml., add 10 grams of sodium hydroxide, and evaporate until ammonia ceases to be evolved. Adjust the volume to about 100 ml., and deposit the zinc on the cathode (already covered with copper) as described on p. 250.

The tin may be determined on a separate portion of 5 grams of the alloy as described on p. 371.

PART IV

COLORIMETRIC METHODS

THE determination of a very small quantity, or of the merest trace, of a substance is frequently of the highest importance, and it is often found that the most accurate and by far the easiest method is a colorimetric one. The percentage accuracy obtainable is naturally lower than in the determination of larger quantities by ordinary means. Without special precautions the probable error will be greater than $\pm$ 2 per cent. Colorimetric methods are based on a very simple principle, which the following example may serve to illustrate.

When ammonium thiocyanate is added to a solution of a ferric salt, a red coloration is produced. The colour is perceptible when the solution contains even less than 1 part of iron in 10,000,000 (0·1 mgrm. per litre), and becomes more intense as the quantity of iron is increased. The amount of iron present can be ascertained by finding how much of a very dilute standard solution of a ferric salt must be added to a known quantity of water in order to produce with ammonium thiocyanate, a coloration of equal intensity.

A colorimetric determination occupies but a short time, whereas gravimetric or volumetric methods, if applicable at all, would prove extremely tedious and probably less accurate. Colorimetric methods in general are suitable for the determination of small quantities only. Unless the total amount of substance present is known to be small, the solution containing it should be diluted to a known volume and a suitable portion taken for the analysis.

In many cases the determination is made in a true solution, but, as in the determination of lead as sulphide, the comparison may be carried out in a colloidal solution, provided that this is sufficiently stable, or can be rendered so by the addition of a suitable substance.

In colorimetric determinations it is usually essential (1) that

the solutions to be compared contain as far as possible the same quantities of admixed substances, (2) that they are at the same temperature, (3) that they are diluted to the same volume before adding the reagent, and (4) that the order in which the reacting substances are mixed, and the time allowed before the comparison is made, are as nearly the same as possible ; otherwise serious errors may arise.

A number of examples of the application of colorimetric methods will be found in Part VIII. (Water Analysis).

Methods of Determination

In making a comparison between the solution being investigated and the standard solution, one of the following methods may be adopted. Methods (1) and (4) fulfil most closely the conditions laid down above.

(1) For this method cylinders of colourless glass (Nessler tubes) may be used. These tubes are usually graduated to contain 50 ml. or 100 ml., and the graduation mark must be at the same level in all tubes of equal capacity. In order to exclude side light, it is worth while providing the tubes with opaque covers open at the ends and made from stout brown paper. A glass tube on which a flattened bulb of appropriate size is blown (Fig. 58) should be used for mixing the solutions in the tubes. The colour intensities are compared by holding the tubes close together over a white surface (*e.g.* a sheet of opal glass) and looking down into the tubes. A stand similar to a test-tube rack, having an opal glass base and holes for six Nessler tubes, is obtainable for the purpose.

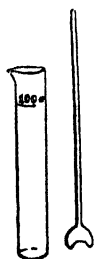



Fig. 58.

There is for each substance a depth of colour which is most suitable for matching. A solution is prepared in a Nessler tube containing the correct amount of standard substances to give this depth, adding the reagents in the prescribed order. A preliminary determination of the strength of the unknown solution is made by adding it from a burette to another Nessler tube containing the reagents diluted with a convenient amount of water until approximately the same depth is obtained. The volume of solution added is observed and the liquid rejected. Into the Nessler tube this volume of the solution is now run,

and the reagents added in the same order as in the case of the standard. The depth of colour obtained will probably be found to be slightly different from that of the standard. Prepare other standards containing slightly more or slightly less of the standard solution, adding the constituents in the same order, until an exact match is obtained.

To most observers the solution in the tube held in the left hand appears slightly darker in colour than that in the right, even when the two tubes are filled with portions of the *same* solution. It is a good plan therefore, in colorimetric comparisons generally, to interchange the tubes, and if the left-hand tube always appears the darker, it may be assumed that the intensities of the colorations are equal.

(2) A fixed amount of the reagent is diluted with a suitable volume of water, and a measured volume of the unknown solution added. An equal amount of reagent in another tube is diluted almost to the same volume, and a standard solution of the substance to be estimated is added until, after mixing, the depth of colour matches that of the unknown.

(3) To a measured quantity of the sample a definite amount of reagent is added, and it is then diluted to some known volume, and placed in a cell with parallel sides. A solution for comparison, having the same total volume, is prepared, using an equal amount of reagent and a measured volume of a standard solution of the substance to be estimated. This solution should be slightly deeper in tint than the one which is being determined. Pour this into a similar rectangular cell of the same dimensions. Add water from a burette to the deeper solution until the colour in the two cells appears to be of equal depth when the cells are viewed from the side.[1] The initial concentrations of the two solutions are directly proportional to the final volumes, provided that the dilution of the darker liquid has not caused any change in the amount of coloured substance present.

(4) In this method a match is obtained by altering the observed length of one of the columns of liquid which is compared with a fixed length of the other. For the method to be accurate, the depth of colour of the two liquids should be nearly equal. The two liquids are placed in two similar tubes, and

[1] Apparatus especially designed for the purpose is described in Hillebrand and Lundell's *Applied Inorganic Analysis*.

the length of the column of the darker solution is reduced until the colour appears equal in both. If the concentrations of the solutions being compared are nearly equal, the ratio of the lengths of the columns after matching will be equal to the inverse ratio of the concentrations. The method is most conveniently carried out in a colorimeter.

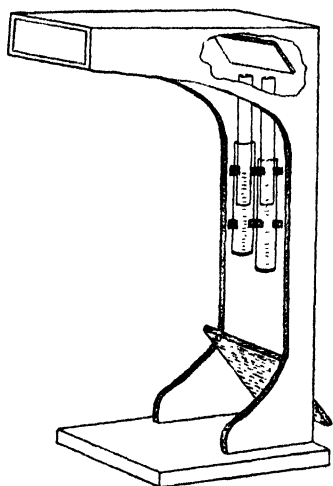



Fig. 59.—The Schreiner Colorimeter.

In the commonest types of colorimeter a plunger tube is used to shorten the observed column of liquid in one of the two comparison vessels, but in some the length of column is reduced by withdrawing liquid from one of the comparison tubes. In the instrument illustrated (Fig. 59), the plunger tube is fixed, and the tube holding one liquid is raised until the depth of colour appears equal to that of the other liquid contained in a similar tube alongside. To compensate for any colour effect due to the glass end of the plunger tube, a similar one is placed in the field of view of the tube containing the paler liquid, but it is not immersed in it. Light is reflected from a mirror near the base of the instrument, and after passing through the two liquids under observation, it is reflected by a mirror placed above them. The coloured solutions are thus observed side by side. Graduations are provided, so that the lengths of the columns viewed may be read.

Iron

A convenient method for the colorimetric determination of iron is based, as already stated, on the red coloration which ammonium thiocyanate gives with a solution of a ferric salt. The solution containing the iron must be acid, and a large excess of the thiocyanate must be used. The red coloration fades slowly on account of the spontaneous decomposition of the ferric thiocyanate. This method is satisfactory in many

cases, but in the presence of phosphates, fluorides, and certain organic acids, the development of colour is seriously affected. Metals which are precipitated by ammonium thiocyanate, and those which give a coloured solution with this reagent, interfere. In such cases the iron must first be separated if ammonium thiocyanate is to be used. The use of thioglycollic acid, described by Lyons (*J. Amer. C. S.*, 1927, vol. 49, p. 1916), makes this separation unnecessary, unless considerable amounts of these metals are present.

Both these methods are described below.

Ammonium Thiocyanate Method

The following solutions are required :—

(1) *Standard Iron Solution.*—Dissolve 0·260 gram of ammonium ferric sulphate in water, add 10 ml. of dilute hydrochloric acid, and dilute to 1 litre. One ml. of the solution corresponds to 0·03 mgrm. of iron.

(2) *Ammonium Thiocyanate Solution.*—Dissolve 50 grams of the pure salt in 100 ml. of water.

Procedure.—The iron must be present as a ferric salt. The best depth of colour for matching is obtained with about 0·15 mgrm. of iron in the final volume contained in the Nessler tube.

Prepare a standard as follows :—Measure with a burette 5 ml. of the standard iron solution into a Nessler tube, add 1 ml. of concentrated hydrochloric acid (free from iron), and dilute to the 100 ml. mark. Add 5 ml. of the ammonium thiocyanate solution, and mix.

Measure 1 ml. of concentrated hydrochloric acid into another Nessler tube, dilute to about 75 ml., and add 5 ml. of the ammonium thiocyanate solution. Now run in the unknown iron solution from a burette until the depth of colour after mixing is approximately equal to that of the standard. Observe the volume of the unknown solution used, and reject the liquid.

Into the Nessler tube run this observed volume of the unknown solution, add 1 ml. of concentrated hydrochloric acid, dilute to the 100 ml. mark, and add 5 ml. of the ammonium thiocyanate. The depth of colour obtained after mixing will probably be slightly different from that of the standard. Prepare other standards for comparison, using less or more of the standard iron solution, adding the constituents in the same

order, until an exact match is obtained. These standards may suitably differ from each other by 0·25 ml.

If a colorimeter is available, the requisite amount of standard solution for comparison is prepared for one of the tubes, and a preliminary test with the unknown solution carried out as described above. Using the amount of the unknown solution required, the second tube is refilled, adding the constituents in the same order as in the preparation of the standard, and making the final volume the same. The tubes are placed in the colorimeter, and the depth of the plunger in the darker liquid is adjusted until a match is obtained. The concentrations of iron in the two solutions are inversely proportional to the lengths of the columns matched.

Exercise.—Determine the amount of ferric salt in a sample of commercial ferrous sulphate or ferrous ammonium sulphate by the thiocyanate method. Dissolve a weighed quantity (1 to 2 grams) in about 0·3N hydrochloric acid, which has been recently boiled and cooled in carbon dioxide, and make up to 100 ml. with the same acid.

Thioglycollic Acid Method

When a mixture of this reagent with a solution of a ferrous salt is made alkaline with ammonia, an intense red coloration is developed. Ferric salts as such do not give this colour, but they are reduced to ferrous salts by excess of the reagent, so that the *total iron present* is estimated. Strong bases discharge the colour, and it is therefore necessary to use ammonia, in which the colour is stable for a considerable time. Chromium and cobalt interfere, and oxidising agents must of course be absent.

Procedure.—A suitable depth of colour for matching is obtained with about 0·15 mgrm. of iron in the final volume contained in the Nessler tube.

Prepare a standard as follows:—Measure 5 ml. of the standard iron solution, as described under the thiocyanate method, into a 100 ml. Nessler tube, add about 75 ml. of distilled water, and 5 ml. of concentrated ammonia. Dilute to 100 ml., add 10 drops of thioglycollic acid, and mix. The full colour does not develop for a minute or two.

The remainder of the process is carried out in an analogous manner to that described under the thiocyanate method.

Nickel

Very minute quantities of nickel may be determined by means of a solution of dimethylglyoxime, which produces a scarlet precipitate with dilute solutions of nickel salts (see p. 327), and gives a pink coloration with traces of nickel. A precipitate separates out on standing, so that the comparison should be made without much delay. The separation of the precipitate can be prevented, and greater sensitivity attained, by adding a hypochlorite. The colour produced under these conditions is an orange shade. A trace of iron does not interfere, but if much is present it must be removed as described under copper (see p. 262). Cobalt and copper also give colorations with the reagent, but interference due to these can be prevented by the addition of sufficient potassium cyanide solution to redissolve their respective cyanides.

The following solutions are required :—

(1) *Standard Nickel Solution.*—Dissolve 0·673 gram of nickel ammonium sulphate in water, and dilute the solution to 1 litre. Dilute 10 ml. of this solution to 100 ml. One ml. of this diluted solution contains 0·01 mgrm. of nickel.

(2) *Dimethylglyoxime Solution.*—Dissolve 1 gram in 100 ml. of absolute alcohol.

Procedure.—The solution must be almost neutral. A suitable depth of colour for matching is obtained with about 0·04 mgrm. of nickel in the final volume of the Nessler tube.

Prepare a standard as follows :—Measure 4 ml. of the standard nickel solution into a Nessler tube, add 10 drops of dilute ammonia by means of a pipette, and 10 drops of a 1 per cent. sodium hypochlorite solution. Dilute to 50 ml., add 5 ml. of the reagent, and mix. The full colour requires a few minutes for development, but remains without change for a long time.

The remainder of the process is carried out in an analogous manner to that described under iron (see p. 257).

Titanium

Hydrogen peroxide produces with an acid solution of titanium sulphate a strong yellow colour, the intensity of which with small amounts of titanium is proportional to the amount of titanium present. The colorimetric method based on this reaction is superior to all others for the determination of a small

amount of titanium, such as that commonly present in silicate rocks or iron ores.

The titanium sulphate solution must contain at least 5 per cent. of sulphuric acid. A mere trace of hydrofluoric acid in either the hydrogen peroxide or the titanium solution renders the results inaccurate. The error introduced by the presence of ferric sulphate, in consequence of its yellow colour, is negligible unless the original substance contains more than 5 per cent. of iron. If necessary, a correction may be applied, as indicated below. Interference due to other metals whose salts are coloured or which give a colour with hydrogen peroxide may in most cases be eliminated by precipitating the titanium with "cupferron." For details, see Taylor-Austin *J.S.C.I.*, 1941, T. 29.

The following solutions are required :—

(1) *Dilute Sulphuric Acid* (5 *per cent.*).—Dilute 30 ml. of concentrated sulphuric acid to 1 litre.

(2) *Standard Titanium Solution.*—Weigh accurately in a platinum crucible 0·3750 gram of pure, dry potassium titanium fluoride, K_2TiF_6. Add concentrated sulphuric acid and evaporate (Fig. 13, p. 29) almost to dryness. Repeat this operation several times until the hydrofluoric acid is completely expelled. Dissolve in a little sulphuric acid and dilute with 5 per cent. sulphuric acid to 250 ml. One ml. of the solution corresponds to 0·5 mgrm. TiO_2.

(3) *Hydrogen Peroxide.*—A 3 per cent. ("ten volume") solution, free from hydrofluoric acid.

Procedure.—A suitable depth of colour for matching is obtained with about 1·5 mgrm. of TiO_2 in the final volume contained in the Nessler tube.

Prepare a standard as follows :—Measure 3 ml. of the standard titanium solution into a 100 ml. Nessler tube, add 5 ml. of hydrogen peroxide, dilute with 5 per cent. sulphuric acid to 100 ml., and mix.

The remainder of the process is carried out in an analogous manner to that described under iron (p. 257).

If the original solution contains ferric sulphate, the requisite amount of iron alum must be added to the standard in order to compensate for the yellow colour of the ferric salt.

Determination of Titanium in Iron Ore.—Weigh accurately

in a platinum crucible about 0·5 gram of the finely powdered ore and fuse it with about 5 grams of dry sodium carbonate as described in detail on p. 341. When the fusion is complete, allow the crucible to become cold, and then place it upright in a covered beaker containing 50 ml. of dilute sulphuric acid. Upset the crucible with a glass rod, and warm gently until the mass is completely detached from the crucible. Remove the crucible and rinse it. Add 3 ml. of concentrated sulphuric acid, and heat until all that is soluble has dissolved. Filter into a 100 ml. graduated flask. After cooling, add 5 ml. of hydrogen peroxide, and dilute to the mark.

Determine the titanium in the solution colorimetrically. In order to correct for the colour of the ferric sulphate in this solution, determine the approximate iron content colorimetrically by diluting 2 ml. with 5 per cent. sulphuric acid to 250 ml. About 5 ml. of this diluted solution should be a suitable volume for the determination of the iron. After ascertaining by trial what aliquot part of the 100 ml. ore solution is required for the titanium determination, calculate the amount of ferric alum equivalent to the iron content in this aliquot part. This quantity of ferric alum must be added to each titanium standard used in matching the solution being determined.

Copper

Potassium ferrocyanide has hitherto been the usual reagent for the colorimetric estimation of copper, but Callan and Henderson (*Analyst*, 1929, vol. 54, p. 650) have shown that sodium diethyldithiocarbamate is a more sensitive reagent for copper, and gives a colour which is easily matched. One part of copper in 50,000,000 of solution gives a definite orange yellow coloration, and the colour is produced in acid, alkaline, and neutral solution. Lead, iron, bismuth, and other heavy metals interfere with the test; and zinc if present in amount greatly exceeding that of the copper. The colour produced is stable for several hours.

The following solutions are required :—

(1) *Standard Copper Solution.*—Dissolve 0·393 gram of pure crystalline copper sulphate, and make up the solution to 1 litre. Dilute 25 ml. of this to 250 ml. One ml. of this solution contains 0·01 mgrm. of copper.

(2) *Sodium Diethyldithiocarbamate.*—Dissolve 0·1 gram in 100 ml. of water.

Procedure.—If iron is present, add 1 ml. of concentrated nitric acid to a measured volume of the solution to be determined, and evaporate to a small bulk. Precipitate the iron by adding a slight excess of ammonia, filter, and wash. Dissolve the ferric hydroxide in dilute nitric acid, reprecipitate with ammonia, filter, and wash. Combine the two filtrates, and dilute to a known volume.

If lead (or bismuth) is present, add a few drops of ferric chloride solution, boil, and precipitate twice with ammonia as above.

A suitable depth of colour for matching is obtained with about 0·05 mgrm. of copper in the final volume in the Nessler tube.

Prepare a standard as follows:—Measure 5 ml. of the standard copper solution into a 100 ml. Nessler tube, add 20 ml. of dilute ammonia, dilute to the mark, add 10 ml. of the reagent, and mix.

The remainder of the process is carried out in an analogous manner to that described under iron (p. 257). If zinc is present, sufficient ammonia must be added to prevent any turbidity developing after the addition of the reagent.

Copper may also be determined colorimetrically in presence of iron by means of hydrogen sulphide, as described under lead, provided that lead and other metals forming sulphides insoluble in acid are absent.

Lead

The most satisfactory method for the determination of a minute quantity of lead depends on the coloration produced when hydrogen sulphide is added to the solution containing it. The solution should be slightly acid—preferably with acetic acid. Copper and other metals that form sulphides insoluble in acid interfere, but dilute solutions of iron salts give no coloration with hydrogen sulphide in presence of acid.

The following solutions are required:—

(1) *Standard Lead Solution.*—Dissolve 0·0915 gram of lead acetate in water, add acetic acid until a clear solution is obtained, and dilute to 1 litre. One ml. of the solution corresponds to 0·05 mgrm. of lead.

(2) *Hydrogen Sulphide Solution.*—Saturate some freshly boiled (and cooled) distilled water with the gas, and transfer the solution to a burette fitted with a cork. Protected in this way from the air, the solution will remain clear for a long time, especially if kept in the dark.

Procedure.—If the solution to be tested is strongly acid, almost neutralise the excess of acid with sodium hydroxide and then add a little sodium acetate.

A suitable depth of colour for matching is obtained with 0·2 mgrm. of lead in the final volume in the Nessler tube.

Prepare a standard as follows :—Measure 4 ml. of the standard lead solution into a 100 ml. Nessler tube, add 2 ml. of dilute acetic acid, 10 ml. of a concentrated solution of sugar, and dilute to 100 ml. Now add 2 ml. of hydrogen sulphide solution, and mix. (The sugar is added in order to prevent the precipitation of lead sulphide on mixing.)

The remainder of the process is carried out in an analogous manner to that described under iron (p. 257).

Bismuth

Bismuth can be determined colorimetrically by means of the yellow colour produced on adding a solution of potassium iodide to an acid solution containing traces of the metal. Silver, lead, and copper interfere, and must be separated first.

The following solutions are required :—

(1) *Standard Bismuth Solution.*—Dissolve 0·125 gram of pure bismuth oxychloride in about 20 ml. of dilute hydrochloric acid in a 100 ml. flask, dilute to the mark, and mix thoroughly. Dilute 10 ml. of this solution to 1 litre, adding about 25 ml. dilute hydrochloric acid before the dilution. One ml. of this solution contains 0·01 mgrm. of bismuth.

(2) *Potassium Iodide Solution.*—Dissolve 4 grams of potassium iodide in about 100 ml. of water. This solution must be freshly prepared.

Procedure.—A suitable depth of colour for matching is obtained with about 0·05 mgrm. of bismuth in the final volume contained in the Nessler tube.

Prepare a standard as follows :—Measure 5 ml. of the standard bismuth solution into a 100 ml. Nessler tube, add about 80 ml. of water, and 10 ml. of the potassium iodide solution. Dilute to 100 ml., and mix.

The remainder of the process is carried out in an analogous manner to that described under iron (p. 257).

If lead is present, add about 3 grams of tartaric acid, and excess of dilute sulphuric acid to a measured volume of the bismuth solution. After standing a few hours, filter, add 10 ml. of concentrated nitric acid to the filtrate, and evaporate as far as possible on a water-bath. Heat carefully over a small flame until thick white fumes of sulphuric acid are evolved in order to eliminate tartaric and nitric acids. Dilute to a suitable volume, and determine the bismuth as above.

If copper is present, add a few drops of a solution of aluminium sulphate, boil, and precipitate the aluminium and bismuth with ammonia. Dissolve the precipitate in hot dilute hydrochloric acid, and reprecipitate. Dissolve the second precipitate in dilute hydrochloric acid, dilute to a suitable volume, and determine the bismuth as above.

Manganese

The gravimetric determination of a small amount of manganese in a complex substance is seldom accurate, largely owing to the difficulty of completely separating it from the other constituents of the substance. As a rule, it is possible to determine the manganese in a separate portion of the substance by a colorimetric method.

The method depends upon the conversion of the manganese into permanganate by means of a suitable oxidising agent. Of those which have been used, potassium periodate is the most satisfactory, the oxidation being complete, and the permanganate solution formed being very stable in the presence of excess of the periodate.

The following solutions are required :—

(1) *Standard Manganese Solution.*—Dissolve 0·144 gram of pure potassium permanganate in about 100 ml. of water, and pass a current of sulphur dioxide through the solution until it becomes clear and colourless. Boil the solution until free from sulphur dioxide, cool, and dilute to 1 litre. One ml. of the solution corresponds to 0·05 mgrm. of manganese.

(2) *Mixture of Sulphuric and Phosphoric Acids.*—To about 150 ml. of water, add 70 ml. of concentrated sulphuric [or nitric acid], and 35 ml. of syrupy phosphoric acid. Cool,

and dilute to 250 ml. (The phosphoric acid eliminates any colour due to iron if present.)

Procedure.—If chlorides or reducing agents are present in the solution under test, they must be removed by evaporation with sulphuric and nitric acids, and the solution diluted again to the original volume.

A suitable depth of colour for matching is obtained with about 0·3 mgrm. of manganese in the final volume in the Nessler tube.

Prepare a standard as follows :—Measure 6 ml. of the standard manganese solution into a small conical flask, add 25 ml. of the acid mixture, 15 ml. of water, and 0·3 gram of solid potassium periodate. Heat, and keep the solution boiling for at least five minutes.

Into another conical flask of the same size, measure 25 ml. of the acid mixture, 10 ml. of water, and add 0·3 gram of potassium periodate. Heat to boiling, and run in a measured volume of the unknown solution from a burette. After five minutes' boiling, make a rough comparison of the colour in the two flasks. If the colour in the second flask is lighter, run in more of the unknown solution until, after a further five minutes' boiling, a darker colour than that of the standard is obtained. Cool, transfer the solutions to Nessler tubes, and dilute both to 50 ml.

By means of a graduated pipette, withdraw some of the darker solution until an approximate match is obtained. From the ratio of the volume of the darker solution left to the 50 ml. of the standard, calculate the approximate concentration of manganese in the unknown solution. Make up three other solutions of the unknown under the same conditions as the standard, one containing the same amount as the standard as deduced from this calculation, and the others 5 per cent. more and 5 per cent. less respectively. Cool these, dilute them in Nessler tubes to 50 ml., and observe which gives the best match with the standard.

Exercise.—Determine the percentage of manganese in a sample of commercial lime. Before commencing the determination, make a rough experiment, using about 1 gram of the lime, in order to ascertain approximately how much manganese is present. Dissolve the lime in nitric acid, and use in the estimation a mixture of nitric and phosphoric acids.

Aluminium

In acetic acid solution aluminium salts form with aurin tricarboxylic acid a lake with a deep rose colour, which in very dilute solution gives a coloured liquid. This reagent can therefore be used for the colorimetric determination of traces of aluminium. Iron and beryllium salts also form a strongly coloured lake, so that if even traces of these metals are present they must be removed. Reducing agents must also be absent. The reagent itself imparts a faint orange tint to the solution, and this can be almost eliminated by the addition of ammonium hydroxide and ammonium carbonate ; but there is no difficulty in matching solutions without the addition of these reagents.

The following solutions are required :—

(1) *Standard Aluminium Solution.*—Dissolve 0·88 gram of potash alum in water, add 10 ml. of concentrated hydrochloric acid, and dilute to 1 litre. One ml. contains 0·05 mgrm. of aluminium.

(2) *Ammonium Acetate Solution.*—Dissolve 20 grams of ammonium acetate in water, and dilute to 100 ml.

(3) *Hydrochloric Acid Solution.*—This should be approximately normal.

(4) *Ammonium Aurin Tricarboxylate* (*Aluminon*).—Dissolve 0·2 gram of aluminon in 100 ml. of water.

Procedure.—If iron is present, add to a measured quantity of the unknown solution excess of pure sodium hydroxide, boil, filter, and wash the precipitate. Redissolve this in the smallest possible amount of hydrochloric acid, and reprecipitate, filter, and wash as before. Mix the filtrates and washings, make just acid with acetic acid, and evaporate, finally making up to the same volume as originally taken.

A suitable depth of colour for matching is obtained with about 0·3 mgrm. of aluminium in the final volume in the Nessler tube.

Prepare a standard as follows :—Measure 6 ml. of the standard aluminium solution into a small flask, add 2 ml. of normal hydrochloric acid, 10 ml. of ammonium acetate solution, 30 ml. of water, and 5 ml. of the reagent. Heat to boiling.

Into another flask of the same size, measure 2 ml. of normal hydrochloric acid, 10 ml. of ammonium acetate solution, 35 ml. of water, and 5 ml. of the reagent. Heat to boiling, and

run in the unknown solution from a burette until the colour is slightly deeper than that of the hot standard. Cool both solutions, transfer to Nessler tubes, and dilute each to 100 ml.

The remainder of the process is carried out in an analogous manner to that described under manganese (p. 265).

Use of Colorimeter

Any of the above determinations may be made more conveniently and more accurately with the colorimeter described on p. 256. This applies especially to the estimations of aluminium and manganese, in which the special procedure that has to be adopted makes the process of matching more difficult.

Vanadium in Steel

When hydrogen peroxide is added to a solution containing traces of vanadic acid, a reddish-brown colour is produced due to the formation of pervanadic acid. From the depth of this colour the amount of vanadium in a sample of steel can be estimated. It is necessary to compensate for any colour due to the presence of other elements.

A standard ammonium meta-vanadate solution is prepared by dissolving 1·148 gram of the salt, NH_4VO_3, in water, and making up to 1 litre. One ml. of this solution contains 0·5 mgrm. of vanadium.

Procedure.—Dissolve 1 gram of the sample in 15 ml. of 1 : 5 sulphuric acid in a 400 ml. beaker of tall form. When solution is complete, oxidise with 10 ml. of concentrated nitric acid, and boil until free from oxides of nitrogen. Dilute to 150 ml. with hot water, boil, and add carefully a saturated solution of potassium permanganate until a pink colour persists or a precipitate is formed. Boil for five minutes. (If tungsten is present, filter off the mixed tungstic acid and manganese dioxide through an asbestos filter.) Add sulphurous acid in slight excess, and boil until free from sulphur dioxide. Cool, add 5 ml. of syrupy phosphoric acid, and 7 ml. of 10-volume hydrogen peroxide.

The standard solution for comparison is prepared by treating a vanadium-free steel, to which has been added nickel, chromium, cobalt, and molybdenum to the same percentage as in the sample, in the same way as above.

(Nickel, chromium, and cobalt are added as sulphates. Molybdenum is added as ammonium molybdate, when the steel contains more than 0·5 per cent. of molybdenum.)

Transfer the solutions to two graduated 200 ml. comparison cylinders, and add, a little at a time, standard ammonium meta-vanadate to the standard solution until the colour matches that of the solution under test. The liquid must be shaken well, and allowed to stand for two minutes after each addition for the full colour to develop. From the volume of the standard ammonium meta-vanadate added, calculate the percentage of vanadium in the sample of steel.

Ammonia

The colorimetric determination of ammonia is carried out almost exclusively in connection with water analysis, and it has therefore been included in Part VIII, p. 448.

Phosphate

Traces of phosphate may be determined by the formation of an intense blue colour on adding stannous chloride to the solution, in presence of ammonium molybdate. The presence of ferric iron causes a positive error, but if this is first reduced to the ferrous state, iron is permissible up to about 50 parts per million in the final volume of the solution. Arsenic, vanadium, and silicic acid must be absent.

The experimental conditions described must be closely adhered to, as variation in the amount of stannous chloride or ammonium molybdate causes considerable changes in the colour intensity with the same amount of phosphate.

The following solutions are required :—

(1) *Ammonium Molybdate.*—Dissolve 0·25 gram of ammonium molybdate in about 125 ml. of water, add 20 ml. of dilute sulphuric acid and dilute to a 250 ml. in a graduated flask.

(2) *Stannous Chloride.*—Dissolve 0·25 gram of pure tin in 5 ml. of concentrated hydrochloric acid diluted with an equal volume of water, adding a small crystal of copper sulphate and heating to hasten solution. When the tin has dissolved, filter into a 250 ml. graduated flask, and make up to the mark with recently boiled and cooled water.

(3) *Standard Phosphate Solution.*—Weigh 0·294 gram of microcosmic salt, dissolve it in water and dilute to 100 ml. in a graduated flask. Dilute 5·0 ml. of this solution to 500 ml. in a graduated flask. One ml. of the diluted solution contains 0·01 mgrm. of phosphorus pentoxide.

Procedure.—The solution of the phosphate to be determined must be almost neutral. A suitable depth of colour for matching is obtained with about 0·04 mgrm. of phosphorus pentoxide in the final volume of 100 ml. in the Nessler cylinder.

Prepare a standard as follows :—Measure 4 ml. of the standard phosphate solution into a Nessler cylinder, add 5 ml. of the ammonium molybdate solution, and dilute to about 90 ml. Add 1 ml. of the stannous chloride solution, dilute to the 100 ml. mark, and mix thoroughly. The colour is fully developed in four minutes, but the comparison of the unknown phosphate solution with a series of standards should be carried out within half an hour of making up the solution.

Make up a preliminary test solution of the unknown phosphate in exactly the same manner as above, using an amount which is believed to contain approximately the same quantity of phosphorus pentoxide as in the above standard. If the phosphate concentration is quite unknown, the amount to be used must be found by several trials. When the amount required to give approximately the same colour as in the above standard is found, a series of suitable standards is prepared having a range which covers the depth of colour in the unknown solution.

DETERMINATION OF THE pH OF A LIQUID BY MEANS OF INDICATORS

It has already been pointed out that indicators undergo a change in colour when a marked alteration occurs in the pH value of a solution containing them (p. 64). Use may also be made of them for the actual determination of pH, as an alternative to an electrometric method described in Part II.

An approximate determination of the pH of the liquid is made by using a mixture of indicators so chosen that a series of different colours is given over a wide range of pH values. A specified amount of the mixture is added to a definite volume

of the solution to be tested, and by reference to a colour chart the *p*H may be judged to about 0·5 of a unit.[1] This may be sufficiently accurate in many cases, but if a more exact determination is required, special solutions must be prepared, mixtures of which have *p*H values including the approximate value of *p*H found. An indicator must then be selected whose range of colour change also contains this *p*H value. The preparation of these solutions, known as "buffer" solutions,[2] and lists of indicators with their *p*H ranges will be found in books dealing specifically with the measurement of hydrion concentration. A universal buffer may be obtained from dealers by means of which solutions of any *p*H value between 2·7 and 11·4 may be prepared by simple addition of the requisite amount of standard acid or alkali.

As an example of the procedure to be adopted, a method for determining the *p*H when this lies between 5 and 8 is here described.

Determination of *p*H between the Values 5 and 8

The following solutions are required :—

(1) *Disodium Hydrogen Phosphate.*—Dissolve 23·88 grams of $Na_2HPO_4, 12H_2O$ in water, and dilute to 1 litre. "Chemically pure" crystals, free from efflorescence, are satisfactory. The *p*H of this solution is 9·2.

(2) *Potassium Dihydrogen Phosphate.*—Dissolve 9·08 grams of KH_2PO_4 in water, and dilute to 1 litre. The salt must be free from chloride and sulphate. The *p*H of this solution is 4·5.

[1] Such a mixture and colour chart may be obtained from chemical dealers.

[2] A buffer solution is one whose *p*H is not appreciably altered by the addition of considerable amounts of acids or alkalis. Such a solution is formed when a weak acid, for example acetic acid, is added to a solution of one of its salts, say sodium acetate. The liquid will contain a large amount of acetate ions, which will combine with any hydrions added, forming unionised acetic acid ; and it also contains a considerable amount of unionised acetic acid, which will provide hydrions to combine with any hydroxyl ions added. In this way any fall or rise in *p*H is hindered. The addition of a salt such as potassium dihydrogen phosphate, KH_2PO_4, will also buffer an aqueous solution ; for the H_2PO_4 ions will take up added hydrions to give unionised H_3PO_4, and also provide hydrions to neutralise hydroxyl ions added.

Suitable indicators for the *p*H range 5 to 8 are :—

Indicator.	*p*H range.	Colour change.	Concentration of solution.
Methyl red . .	4·4 - 6·2	Red—yellow	0·1% in 60% alcohol
Bromo-cresol purple .	5·2 - 6·8	Yellow—purple	0·05% in 20% alcohol
Bromo-thymol blue .	6·0 - 7·6	Yellow—blue	0·05% in 20% alcohol
Phenol red . .	6·8 - 8·4	Yellow—red	0·05% in 20% alcohol

Procedure.—Measure 50 ml. of the solution to be tested into a Nessler tube, and add 1 ml. of the appropriate indicator selected from the above list. Into a second Nessler tube, measure 25 ml. of the potassium dihydrogen phosphate, or of the disodium hydrogen phosphate, selecting that solution which must be in excess, as shown by the tables below. Add 1 ml. of the indicator, and run in from a burette the other phosphate solution until an approximate match in colour is obtained. Read the volume added and reject the liquid. Prepare a fresh standard, taking proportional amounts of the two phosphate solutions such that the total volume will be approximately 50 ml., add the indicator, and make the final adjustment by addition of one or other of the phosphate solutions as required to obtain an exact match. The *p*H may then be found by reference to the tables.

TABLE I.

(*p*H 5 - 6·8).

Volume of KH_2PO_4 solution taken = 25 ml.

Volume of Na_2HPO_4 solution added.	*p*H.
0·3	5·0
0·6	5·3
1·7	5·7
2·2	5·8
3·6	6·0
4·5	6·1
6·1	6·2
7·3	6·3
9·2	6·4
12·3	6·5
15·2	6·6
19·2	6·7
24·2	6·8

TABLE II.

(*p*H 6·9 - 8).

Volume of Na_2HPO_4 solution taken = 25 ml.

Volume of KH_2PO_4 solution added.	*p*H.
19·1	6·9
15·8	7·0
12·9	7·1
9·3	7·2
7·2	7·3
5·6	7·4
4·5	7·5
3·7	7·6
3·15	7·7
2·35	7·8
1·8	7·9
1·4	8·0

Procedure in the Case of a Slightly Coloured Liquid.—In this case, it is necessary to compensate for the colour of the liquid by matching the solutions in 50 ml. Nessler tubes, arranged as shown in Fig. 60. The light that illuminates the

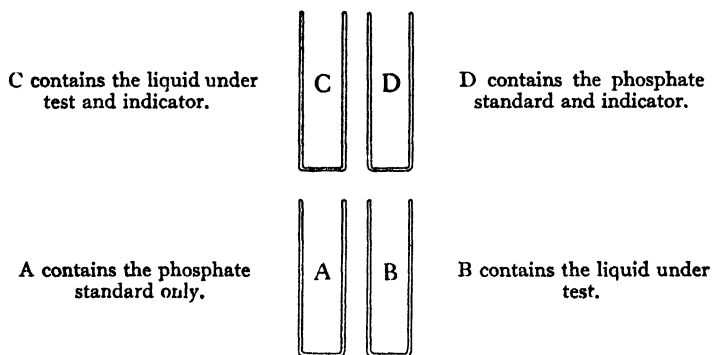



FIG. 60.

phosphate standard in D is made to pass also through the tube B containing the liquid under test (without indicator), whilst the light that reaches the eye through the liquid under test (with indicator) in C passes also through a column of phosphate standard in A.

DETERMINATION OF TRACES OF ARSENIC BY A MODIFIED GUTZEIT METHOD

The following method may be used for the detection and estimation of small quantities of arsenious oxide, the least amount that can be estimated being of the order of 0·001 mgrm. The arsenic is converted to arsine, which gives, on discs of filter paper impregnated with mercuric chloride, a yellow stain with small amounts of arsine, changing to brown as the amount of arsine increases. The stain obtained is compared with a series of stains produced by the use of known amounts of arsenic. The reduction to arsine is effected by nascent hydrogen generated electrolytically (preferably on a mercury cathode), or more simply by the action of hydrochloric acid on " arsenic-free " zinc. The stains may be intensified and made permanent by soaking the discs in a solution of potassium iodide.

The following materials are required :—

(1) *Standard Arsenic Solution.*—Weigh out 0·05 gram of pure arsenious oxide into a small beaker, and dissolve it in a few millilitres of dilute sodium hydroxide solution. Acidify the solution with hydrochloric acid, and make up to 1 litre in a standard flask. Dilute 10 ml. of this solution to 250 ml. in another standard flask. One ml. of this last solution contains 0·002 mgrm. of As_2O_3.

(2) *Lead Acetate Papers.*—Cut several pieces of filter paper 10 by 5 cm., and soak them in a 10 per cent. solution of lead acetate in recently boiled water. Dry the papers, and keep them in a closed tube.

(3) *Mercuric Chloride Papers.*—Cut several strips of filter paper 2·5 cm. in width, and soak them in a saturated solution of mercuric chloride. Place them on a dry filter paper to remove excess liquid, and dry them at about 60° in the dark. Keep these in a closed tube in the dark.

Procedure.—Fit a wide-mouthed bottle of 110 to 120 ml. capacity with a rubber stopper through which is passed a glass tube 20 cm. in length, and 6·5 mm. in internal diameter. One end of the glass tube must have been drawn out to a diameter of about 1 mm., and a hole blown in the side of the tube as near to this end as possible. The tube is inserted so that the hole is just below the lower surface of the stopper. Care must be taken to see that the constricted end of the tube will be above the level of the liquid in the bottle when about 70 ml. has been added. Carefully bore holes of 6·5 mm. diameter as nearly centrally as possible through two rubber stoppers of 2·5 cm. diameter at the wider end, the boring being commenced at the wider ends. Insert the upper end of the glass tube, which must have been previously ground flat on a fine carborundum stone, into one of the rubber stoppers so that the ground end of the tube is flush with the wider end of the stopper. Roll up one of the prepared lead acetate papers in the form of a cylinder 10 cm. in length, and place it inside the glass tube so that the upper end is not less than 2·5 cm. below the top of the tube. This paper serves to remove any hydrogen sulphide which would produce a stain on the mercuric chloride paper. Cut a disc of 2·5 cm. diameter from a piece of the mercuric chloride paper, and place it on the rubber stopper centrally over the glass tube. Attach the other rubber stopper with the

wide end downwards, so that the holes in the two stoppers are in line, by means of two strong rubber bands. This arrangement ensures that the gas generated in the bottle will pass through the disc.

Prepare a series of standards as follows :—Place 10 grams of "arsenic test" zinc in the bottle, and add a few small crystals of stannous chloride. Add 2 ml. of the standard arsenic solution, and then approximately 60 ml. of 2N hydrochloric acid (free from arsenic), and at once insert the stopper with the tube fitted as above. Place the bottle in a large beaker or jar containing water at room temperature, and allow the reaction to proceed for an hour. Remove the mercuric chloride paper disc, and immerse it in a 10 per cent. solution of potassium iodide until the red colour of mercuric iodide at first produced disappears, leaving a brown stain. Allow the disc to dry in the dark on a sheet of filter paper, and number it when dry. Repeat the procedure, increasing the amount of arsenic solution used by 2 ml. each time, and using fresh mercuric chloride and lead acetate papers, and fresh zinc and hydrochloric acid. A series of five discs thus prepared will be sufficient.

If the arsenic content of the liquid to be investigated is entirely unknown, a preliminary test must be carried out starting with one millilitre of the solution, and examining the stain at the end of 15 minutes. If this is not clearly within the range of standards, fresh tests must be made with different amounts of the unknown solution, the hydrochloric acid and zinc being renewed when necessary. When a suitable amount of the unknown arsenic solution has been decided upon, the actual determination must be carried out exactly as described for the preparation of the standards.

PART V

SYSTEMATIC QUANTITATIVE ANALYSIS

ALUMINIUM

In the analysis of a complex mixture, iron and aluminium are separated from all other metals before separation from one another, and are obtained finally as a mixture of ferric oxide and alumina. The iron in the mixed oxides may be determined volumetrically and the aluminium found by difference.

Forms in which Aluminium is precipitated

Aluminium Hydroxide.—This is the easiest method for the determination of aluminium, but is limited in applicability on account of the general insolubility of metallic hydroxides. For details of the procedure, see p. 229.

Basic Aluminium Acetate.—The method serves to separate aluminium (and iron) from nickel, cobalt, manganese, zinc, calcium, and magnesium.

Aluminium Phosphate.—This method is of special value for the separation of aluminium from iron.

Aluminium Oxinate. — By the use of this method aluminium may also be determined volumetrically.

Determination of Aluminium (and Iron) by the Basic Acetate Method

Outline of Method.—The solution is neutralised and largely diluted. Ammonium acetate is added and the solution boiled, whereby basic aluminium and ferric acetates are precipitated. After a second precipitation by ammonia, the precipitate is ignited and the mixture of Fe_2O_3 and Al_2O_3 is weighed. The Fe_2O_3 in the mixed oxides is then determined and the Al_2O_3 found by difference.

Basic Aluminium Acetate is a bulky, gelatinous precipitate, insoluble in water or in slightly alkaline solutions. It probably varies considerably in composition according to the method

of preparation. Unless precipitated under the exact conditions given below, it forms a jelly-like mass which cannot be filtered. It is readily soluble in all acids. It occludes to some extent all soluble salts that may be present in the solution, and these cannot be completely removed by washing. If washed with water, it becomes more gelatinous and chokes the pores of the filter.

On ignition it is completely converted into Al_2O_3, but if the solution contained alkali salts, the precipitated basic acetate is contaminated with occluded alkali salts, and the oxide obtained is also impure.

Basic Ferric Acetate corresponds closely in properties with the aluminium salt, but is less soluble in acetic acid.

Procedure.—The basic acetate method is never used unless it is necessary to separate iron and aluminium from other metals. In the following description of the method it is therefore assumed that a separation of iron and aluminium from other metals, such as manganese, is desired.

Introduce the solution, which should contain no sulphate, into a beaker of at least 750 ml. capacity, and to the cold solution add ammonia cautiously, with constant stirring, until a slight *permanent* precipitate is produced. Then add dilute hydrochloric acid, drop by drop, stirring for about a minute after each drop, until the precipitate is just redissolved. Unless the amount of iron is small, the solution at this stage should be clear brown in colour—if it is yellow, too much acid has been added. Add 3 grams of ammonium acetate dissolved in a little water. If the conditions have been correctly observed, no precipitate will form at this stage, but the solution will become darker and redder in colour. Dilute with hot water to about 400 ml., and heat until boiling. *Boil for one or two minutes only, and then filter as quickly as possible through an 11-cm. paper, using slight suction.* (If the solution is boiled for more than two minutes, or is allowed to cool before filtration, the precipitate becomes so gelatinous that filtration is almost impossible.)

The precipitate is mainly basic ferric and aluminium acetates, but contains also occluded salts. Wash twice with hot water and then redissolve the precipitate by pouring hot dilute nitric acid on it without removal from the filter paper. Wash the paper once with hot dilute nitric acid and then with

hot water. Add 2 ml. of concentrated nitric acid to the solution, and reprecipitate with a slight excess of ammonia. Heat until boiling, filter, and wash thoroughly with hot water. (Combine the two filtrates for the determination of manganese, etc.)

Incinerate the filter paper together with the precipitate in a platinum crucible without previous drying, ignite over a Méker burner, and weigh the mixture of ferric oxide and alumina.

Fuse the mixed oxides with potassium pyrosulphate (p. 387), determine the iron volumetrically, and calculate the weight of ferric oxide equivalent to it. The difference between this and the weight of the mixed oxides is the weight of the alumina.

Determination of Aluminium as Aluminium Phosphate and its separation from Iron

OUTLINE OF METHOD.—The aluminium is precipitated in presence of acetic acid by boiling the solution with sodium phosphate and sodium thiosulphate. The precipitate is ignited, and is weighed as $AlPO_4$. The iron in the filtrate is precipitated as sulphide, converted to hydroxide, and weighed as Fe_2O_3.

Procedure.—To the acid solution (which should not contain more than 50 mgrms. of aluminium, and may also contain iron), add about 2 grams of sodium phosphate, and then ammonium carbonate until a permanent precipitate is obtained. Redissolve the precipitate in dilute hydrochloric acid and add 1 ml. in excess. Dilute the solution to about 300 ml., add about 5 grams of sodium thiosulphate, heat until boiling, and add 20 ml. of dilute acetic acid. Boil for twenty minutes in order to coagulate the precipitated sulphur and to reduce the iron to the ferrous condition. (Ferrous phosphate is not precipitated in presence of acetic acid.)

Filter, and wash with hot water. Dry the precipitate (partially at least) and incinerate the filter together with the precipitate. Ignite and weigh the aluminium phosphate obtained.

If iron is to be determined in the filtrate, evaporate to about 150 ml., and precipitate the iron by the addition of a slight excess of ammonium sulphide. Filter, and wash the ferrous sulphide thoroughly with a dilute solution of ammonium sulphide to prevent oxidation. Dissolve the precipitate on the filter with hot dilute hydrochloric acid, and wash the filter with hot water. To recover traces of iron ignite the filter paper,

and after the carbon has burned away extract the ash with a little warm concentrated hydrochloric acid; dilute, filter through a small filter paper, and add the filtrate to the main iron solution. Boil to expel hydrogen sulphide, oxidise with nitric acid, precipitate the iron as ferric hydroxide, and weigh as ferric oxide as described on p. 225.

Iron may also be separated from aluminium by precipitation of the former with cupferron as described on p. 308.

Determination of Aluminium by Means of Oxine

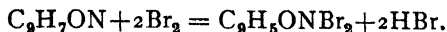
Oxine, 8-hydroxy-quinoline, HOC_9H_6N, gives sparingly soluble precipitates under suitable conditions with many metals, the hydrogen of the hydroxyl group being replaced. The precipitates are easily filtered, and if dried at definite temperatures are of constant composition. Although the reagent is not specific, by adjustment of the *p*H of the solution certain metals may be separated quantitatively from mixtures containing them.

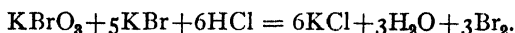
Instead of weighing the precipitates, the metal may be indirectly determined by a volumetric method, the precipitate being decomposed by hydrochloric acid, and the oxine titrated by means of a standard bromate-bromide solution.

Procedure.—Weigh out accurately an amount of alum which does not contain more than 0·03 gram of aluminium. Dissolve this in about 100 ml. of water in a 250 ml. beaker. Heat almost to boiling, clear the solution if necessary by the cautious addition of two or three drops of dilute sulphuric acid, and run in from a burette an excess of a solution of the reagent prepared by warming 2 grams of oxine with 6 ml. of glacial acetic acid and 10 ml. of water, and finally diluting to 100 ml. One ml. of this solution must be added for each mgrm. of aluminium present. Now add a 2N solution of ammonium acetate until a precipitate remains on stirring, and then add a further 30 ml. of this solution. After the precipitate has settled the supernatant liquid should be yellow in colour, indicating the presence of oxine in excess. Filter the warm solution through a Gooch or No. 3 sintered glass crucible, and wash thoroughly with hot water, or, preferably, with a hot saturated solution of aluminium oxinate. Dry at 120°, cool, and weigh as $Al(OC_9H_6N)_3$.

Instead of drying and weighing the precipitate, the aluminium may be determined indirectly by the following volumetric method.

When oxinates are dissolved in hydrochloric acid, free oxine is formed, which will react with bromine in accordance with the following equation :—

$$C_9H_7ON + 2Br_2 = C_9H_5ONBr_2 + 2HBr.$$

Instead of titrating with a standard solution of bromine, it is better to use a mixture of potassium bromate with excess of potassium bromide which in the acid solution reacts as follows—

$$KBrO_3 + 5KBr + 6HCl = 6KCl + 3H_2O + 3Br_2.$$

From the volume of standard bromate used the amount of oxine and therefore the weight of metal present can be calculated.

The standard solution of potassium bromate, which should be decinormal with respect to the bromine liberated, is prepared by dissolving 0·6959 grams of potassium bromate (M/240), together with 3 grams of potassium bromide in water, and making up to 250 ml.

The presence of free bromine showing the end-point of the titration may be indicated by the change in colour of indigo carmine, but it is far more satisfactory to run in a slight excess of the standard bromate-bromide solution, determining this excess by addition of potassium iodide, followed by titration of the iodine liberated with thiosulphate.

The precipitate is dissolved by pouring warm 5N hydrochloric acid through the crucible, stirring with a short glass rod until solution is complete and washing thoroughly with the warm acid, using in all about 75 ml. Cool, and make up to 100 ml. in a graduated flask.

Displace the air from a 300 ml. conical flask by putting into it 2 grams of sodium bicarbonate, and adding 25 ml. of dilute hydrochloric acid. To this add a measured volume of the oxinate solution containing not more than 0·01 gram of aluminium, and run in the potassium bromate-bromide solution from a burette until, *after standing for a few minutes*, a drop removed by a glass rod gives a blue colour with starch-potassium iodide paper (p. 160). When this is the case, note the volume of the bromate solution which has been added. Add 1 gram of potassium iodide, and titrate the iodine liberated by the

excess of bromine with N/10 sodium thiosulphate, adding starch rather earlier than usual since the colour of the solution at the end-point is distinctly yellow. Repeat the titration using an excess of only about 1 ml. of the bromate-bromide solution, as a larger excess may result in the loss of bromine. Deduct the volume of the bromate solution equivalent to the thiosulphate used from the volume originally run in, and calculate the aluminium. One ml. of bromate solution is equivalent to 0·225 mgrm. of aluminium.

AMMONIUM

Ammonia, whether as free ammonia or as an ammonium salt, is determined volumetrically. For details, see pp. 91 to 95.

A colorimetric method for the determination of traces of ammonia is described on p. 448.

ANTIMONY

On account of their comparative simplicity and greater accuracy, volumetric methods for the determination of antimony (see pp. 115, 153, and 164) are preferable to any gravimetric method. The bromate method (p. 164) is applicable to mixtures containing antimony, tin, and arsenic.

The gravimetric determination of antimony is a matter of some difficulty, since in ordinary practice the problem involves the separation of antimony from other elements such as arsenic, with similar chemical properties.

In the analysis of a complex mixture, antimony is usually precipitated as sulphide, together with other metals of the copper and arsenic group.

Antimony Sulphide.—From a hot solution of an antimonious salt, hydrogen sulphide precipitates an orange precipitate of antimonious sulphide which is often contaminated with penta-sulphide or with free sulphur.

Antimony sulphide is readily soluble in alkali hydroxides or sulphides, and in ammonium sulphide. The solubility is inappreciable in cold hydrochloric or sulphuric acid (saturated with hydrogen sulphide) up to about 4N solution. No antimony is precipitated by hydrogen sulphide from a 7N hydrochloric acid solution, and a complete separation from arsenic may be obtained by precipitating the arsenic from a strongly acid

solution (two-thirds concentrated hydrochloric acid, by volume) to which about 3 grams of tartaric acid have been added. The arsenic sulphide is filtered and washed with hydrochloric acid (2 : 1). The antimony sulphide is then precipitated by diluting the filtrate with double its volume of warm water and again saturating with hydrogen sulphide. The precipitate is allowed to settle ; the supernatant liquid is filtered through a hardened paper, and the precipitate is washed by decantation with dilute acetic acid containing hydrogen sulphide. The filter paper is then opened out on the concave side of a clock-glass, and the sulphide is rinsed from it, into the beaker containing the main part of the precipitate, with hydrochloric acid (2 : 1) in which some potassium chlorate has been dissolved. The contents of the beaker are heated until the precipitate has dissolved, and, after expelling chlorine, the antimony is determined volumetrically.

ARSENIC

Arsenic may be determined volumetrically as described on pp. 152 and 165.

Forms in which Arsenic is precipitated

Arsenic Sulphide.—This method gives accurate results if all the arsenic is in the pentavalent state. The solution, cooled in ice, should be slowly diluted with twice its volume of concentrated hydrochloric acid and saturated with hydrogen sulphide. After filtration through a Gooch or sintered glass crucible, the precipitate should be washed with water, dried at 105° to 110°, and weighed as As_2S_5.

Magnesium Ammonium Arsenate.—The arsenic must be present as arsenate.

Determination as Magnesium Ammonium Arsenate

OUTLINE OF METHOD.—The arsenic is precipitated by "magnesia mixture" in presence of a large excess of ammonia, dried at 110°, and weighed as $MgNH_4AsO_4$.

Magnesium Ammonium Arsenate is a white, crystalline precipitate, slightly soluble in water and somewhat less soluble in ammonia solution. The precipitated salt contains six

molecules of water of crystallisation, and cannot be completely dehydrated at 100°. At 110°, it quickly becomes anhydrous, and at somewhat higher temperatures begins to decompose. On ignition, it is converted into magnesium pyroarsenate which, however, decomposes slightly and loses weight if the temperature is very high.

The following solution is required for the precipitation :—

Magnesia Mixture.—Dissolve 6 grams of magnesium chloride and 7 grams of ammonium chloride in water, add 10 ml. of concentrated ammonia, and dilute to 100 ml.

Procedure.—Evaporate the arsenate solution to 100 ml. and add 1 gram of ammonium chloride. Run in, drop by drop, 20 ml. of magnesia mixture, stirring briskly, but without touching the beaker with the stirring-rod. Then add 15 ml. of concentrated ammonia and set aside for twelve hours. Decant through a Gooch or fine sintered glass crucible, and bring the precipitate into the crucible with the help of the filtrate. Wash the precipitate with a dilute solution of ammonia (25 ml. of 2N ammonia diluted to 100 ml.) until the filtrate is free from chloride. Avoid over-washing, as the precipitate is appreciably soluble in dilute ammonia. Place the crucible in the air-oven and raise the temperature slowly, drying finally at 110° to 115° until of constant weight.

BARIUM

Forms in which Barium is precipitated

Barium Sulphate.—This is the usual method, and serves for the separation of barium from almost all other metals.

Barium Chromate.—This method is also convenient and accurate. Barium may be separated from strontium by precipitation as chromate from a solution acidified with acetic acid.

Determination of Barium as Sulphate

The solution is made slightly acid with hydrochloric acid, heated until boiling, and the barium precipitated by a hot dilute solution of sulphuric acid. In all other respects the procedure is identical with that adopted for the determination of sulphate (see p. 235).

Determination of Barium as Chromate

OUTLINE OF METHOD.—The barium is precipitated from neutral or slightly acid solution by ammonium chromate. The barium chromate is filtered through a Gooch or sintered glass crucible, washed with hot water, dried, and weighed as $BaCrO_4$.

Barium Chromate is a yellow, finely divided precipitate which is very slightly soluble in water. At 18°, 1 litre of water dissolves about 4 mgrms., and the solubility is greater at higher temperatures. It is much less soluble in a dilute ammonium chromate solution. It is appreciably soluble in dilute acetic acid and readily soluble in mineral acids. It can be dried completely at 100°, and may be heated to a red heat without decomposition. Heated with organic matter, partial reduction occurs with formation of green chromic oxide; on further ignition with free access of air this is reconverted into chromate.

Procedure.—Neutralise the solution with ammonia or hydrochloric acid, add 1 ml. of acetic acid, and dilute to about 150 ml. Heat the solution until boiling, and precipitate the barium with a hot, dilute solution of ammonium chromate,[1] added through a dropping-tube (p. 236). Place the beaker on the steam-bath until the precipitate settles. Allow to cool. Filter through a Gooch or fine sintered glass crucible. Rinse the beaker, and transfer the precipitate to the crucible with a dilute (0·2 per cent.) solution of ammonium chromate. Wash finally with cold water until the filtrate is free from chromate.

Place the crucible inside a nickel crucible and heat with a small flame until the precipitate has a uniform yellow colour. Weigh the $BaCrO_4$ obtained.

BISMUTH

In the preparation of a solution for analysis it is advisable, if possible, to use nitric acid in preference to hydrochloric or sulphuric acid, in order to simplify the subsequent analysis. In the case of a complex ore or alloy, it is immaterial which acid is used, because it is usually necessary to precipitate the copper and arsenic groups together as sulphides, and afterwards to separate these by appropriate methods.

[1] Dissolve 1·25 gram of ammonium dichromate (free from sulphate) in 100 ml. of water and add sufficient dilute ammonia—about 5 ml.—to give a lemon-yellow coloured solution.

Electrolytic methods for the determination of bismuth have been proposed, but cannot be recommended.

Forms in which Bismuth is precipitated

Basic Bismuth Carbonate.—This method is applicable in presence of sodium, potassium, and ammonium salts only. The results are inaccurate if the solution contains sulphate or chloride.

Metallic Bismuth.—This method is available in presence of zinc, aluminium, sodium, potassium, and ammonium salts.

Basic Bismuth Nitrate.—This method may be used to separate bismuth from all other metals except tin, antimony, and mercury.

Determination of Bismuth as Oxide after Precipitation as Basic Carbonate

OUTLINE OF METHOD.—The bismuth is precipitated by ammonium carbonate as basic bismuth carbonate, which is converted into oxide by ignition and weighed as Bi_2O_3.

Basic Bismuth Carbonate is a granular, white precipitate, which is readily soluble in acids and slightly soluble in ammonia. If precipitated from a solution containing chloride or sulphate, it is always contaminated with basic chloride or sulphate. As these basic salts are not completely converted into oxide by ignition, the method is applicable only in absence of all salts other than nitrate.

Bismuth Oxide, Bi_2O_3, is obtained when the basic nitrate of carbonate is ignited. Complete decomposition occurs on ignition at a low red heat. As the molten oxide attacks porcelain, it is inadvisable to heat above the temperature at which the oxide just melts. The oxide is readily reduced to metal by carbon, and the filter paper should therefore be completely incinerated before the precipitate is brought into the crucible.

Procedure.—Dilute the solution with water to about 50 ml. (a slight turbidity may be produced on dilution). Add ammonium carbonate in slight excess and boil until most of the ammonia is expelled. Filter, wash the precipitate with hot water, and dry. Incinerate the filter paper apart from the precipitate in a porcelain crucible, and oxidise any reduced oxide with nitric acid (compare p. 232). Transfer the main

precipitate to the crucible and heat with a moderate flame—the heat being so regulated that the bismuth oxide is barely fused—and weigh as Bi_2O_3.

Determination of Bismuth as Oxide after Precipitation as Metal

OUTLINE OF METHOD.—The bismuth is precipitated as metal by formaldehyde and alkali. The precipitated metal, which is usually contaminated with alkali, is dissolved in dilute nitric acid and reprecipitated as carbonate. By ignition, the carbonate is converted into the oxide, Bi_2O_3.

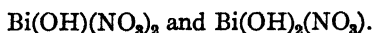
Metallic Bismuth, as obtained by precipitation, is a black, spongy powder which is insoluble in water or in alkaline solutions.

Procedure.—To the bismuth solution, add about 10 ml. of 40 per cent. formaldehyde solution and excess of pure 10 per cent. sodium hydroxide solution. Warm on the steam-bath. When the precipitate has settled and the supernatant liquid has become clear, add a further 5 ml. of formaldehyde and a few millilitres of sodium hydroxide. Heat the solution until boiling, and press together with a glass rod the spongy precipitate of metal, in order to facilitate filtration. Filter, wash thoroughly with hot water, and then dissolve the precipitate with a little hot, dilute nitric acid. Wash the filter paper several times with hot, dilute nitric acid. Precipitate the bismuth as basic carbonate and convert to oxide, as described above.

Determination of Bismuth as Oxide after Precipitation as Basic Nitrate

OUTLINE OF METHOD.—The bismuth is obtained in solution as nitrate, and is precipitated as the basic nitrate by large dilution and neutralisation. The basic nitrate is converted into oxide by ignition, and weighed as Bi_2O_3.

Basic Bismuth Nitrate is usually a mixture of—

$$Bi(OH)(NO_3)_2 \text{ and } Bi(OH)_2(NO_3).$$

It is practically insoluble in cold water, and still less soluble in a very dilute solution of ammonium nitrate. It is readily soluble in acids unless extremely dilute; in the precipitation, however, the solution should still contain a trace of acid, otherwise other metals are precipitated with the bismuth. If

precipitated from a solution containing more than a trace of chloride, the precipitate is contaminated with bismuth oxychloride which is not completely converted into oxide by ignition.

Bismuth Oxide. — The properties of bismuth oxide are described on p. 284.

Procedure.—The bismuth solution must not contain more than a trace of chloride; if it contains chloride in quantity, add 5 ml. of concentrated nitric acid and evaporate until of syrupy consistency; then add a further 5 ml. of nitric acid and again concentrate the solution. After this treatment the solution will be practically free from chloride.

To the bismuth nitrate solution, contained in a 700-1000 ml. beaker, add 500 ml. of water and 5 ml. of methyl orange solution. (Partial precipitation of the basic nitrate usually occurs on dilution.) Add ammonia drop by drop, with constant stirring, until the pink colour is almost, but not quite, discharged. Set the solution aside for one hour, and then filter. Wash with a dilute solution (2 grams per litre) of ammonium nitrate, dry at 100°, remove the precipitate as completely as possible from the paper, and incinerate the paper before addition of the precipitate (p. 219). The ignition of the precipitate should be carried out with the crucible covered, and with a very small flame at first, the temperature being raised slowly. If the heating is rapid, the gases given off during the decomposition of the nitrate carry away mechanically some of the solid. The final temperature should be barely sufficient to fuse the bismuth oxide.

BORATE

Boric acid or the borate in alkali borates, such as borax, may be determined by the volumetric method described on p. 85.

Mineral borates, such as borocalcite or boracite, or alkali borates containing carbonate, are first decomposed by boiling with dilute hydrochloric acid under a reflux condenser. (The condenser is necessary in order to prevent loss of boric acid, which is volatile in steam.) The resulting solution is neutralised with sodium hydroxide using methyl orange as indicator, glycerol or mannitol is added, and the boric acid titrated as described on p. 85.

If appreciable quantities of iron and aluminium are present in the borate, this method of analysis leads to high results, and it is difficult to remove the iron and aluminium without at the same time losing some boric oxide. In order to obtain accurate results in such cases, and also in the analysis of silicates containing boric oxide, a distillation method, depending on the formation of volatile methyl borate, must be used. For a description of this method, see Mellor, *Quantitative Inorganic Analysis*, or Hillebrand and Lundell, *Applied Inorganic Analysis*.

BROMIDE

Bromide is most readily determined volumetrically (see pp. 174 and 178).

Bromide may also be determined gravimetrically by precipitation as silver bromide. The procedure is identical with that adopted for the determination of chloride (see p. 230).

Silver Bromide is less soluble than the chloride. One litre of water dissolves 0·1 mgrm. at 20° and 3·7 mgrms. at 100°. It is insoluble in nitric acid, sparingly soluble in ammonia, and appreciably soluble in concentrated solutions of most salts. It is darkened, with partial decomposition, by light, though to a less extent than the chloride. It melts at 422° and acquires a darker colour. It can be dried completely at 100°.

CADMIUM

The separation of cadmium from certain metals, such as zinc, is a matter of some difficulty, and for methods of analysis applicable to complex ores or alloys, reference should be made to larger text-books. The analysis of Wood's alloy (tin, lead, cadmium, and bismuth) is described on p. 373.

Forms in which Cadmium is precipitated

Metallic Cadmium (Electrolytic).—This is a convenient and accurate method. For details, see p. 249.

Cadmium Sulphide.—This method serves to separate cadmium from metals of the iron, zinc, and calcium groups. If other members of the copper group are present, further treatment is necessary.

Determination of Cadmium as Sulphate after Precipitation as Sulphide

OUTLINE OF METHOD.—The solution is acidified with sulphuric acid, and the cadmium is precipitated with hydrogen sulphide. The cadmium sulphide is dissolved in hydrochloric acid, the solution evaporated to dryness with sulphuric acid, and the residue, $CdSO_4$, is weighed.

Cadmium Sulphide is a yellow precipitate, insoluble in dilute acids or alkalis. It is readily soluble in concentrated hydrochloric acid. It may be completely precipitated by hydrogen sulphide from a solution that contains, in each 100 ml., 10 to 12 ml. of concentrated hydrochloric acid, or 5 to 7 ml. of concentrated sulphuric acid; under these conditions very little zinc will be precipitated with the cadmium. The precipitate is always contaminated with compounds such as Cd_2Cl_2S or Cd_2SO_4S, and must therefore be converted into cadmium sulphate before weighing.

Cadmium Sulphate is colourless. It may be heated to a temperature approaching redness without decomposition. At a higher temperature it is slowly converted into oxide, becoming first yellow and then dark brown.

Procedure.—To the cadmium solution, add 5 ml. of concentrated sulphuric acid, dilute to 100 ml., and saturate with hydrogen sulphide. Filter, and wash with 5 per cent. ammonium nitrate solution. Dissolve the precipitate in the minimum amount of concentrated hydrochloric acid, wash the filter with hot dilute acid, and transfer the filtrate and washings to a large crucible. Add 0·5 ml. of concentrated sulphuric acid, and evaporate as far as possible on the steam-bath. Place the crucible inside a larger nickel crucible or an air-bath (Fig. 42, p. 213), and heat gently until no more fumes of sulphuric acid are given off. Weigh the $CdSO_4$.

CALCIUM

Calcium may be determined volumetrically by the method given on p. 111.

In gravimetric analysis, calcium is always determined by precipitation as oxalate, after removal of the copper, iron, and zinc groups. (For details, see pp. 237 and 383.)

CARBONATE

Carbonate may be determined either gravimetrically or volumetrically in various ways. Two gravimetric methods are in common use, viz. :—

1. A direct method, in which the carbon dioxide, expelled from the carbonate by the action of acid, is absorbed by soda-lime and weighed.

2. An indirect method in which the loss of weight due to the escape of the carbon dioxide from an apparatus is ascertained.

Direct Method

OUTLINE OF METHOD.—A weighed quantity of the substance is mixed with dilute acid in a small flask connected with a series of drying tubes, and with two absorption tubes containing soda-lime. The soda-lime tubes are weighed before and after the experiment.

The Apparatus (Fig. 61) consists of the following :—

A. A distilling flask, of about 125 ml. capacity, provided with a rubber stopper and dropping-funnel. The stem of

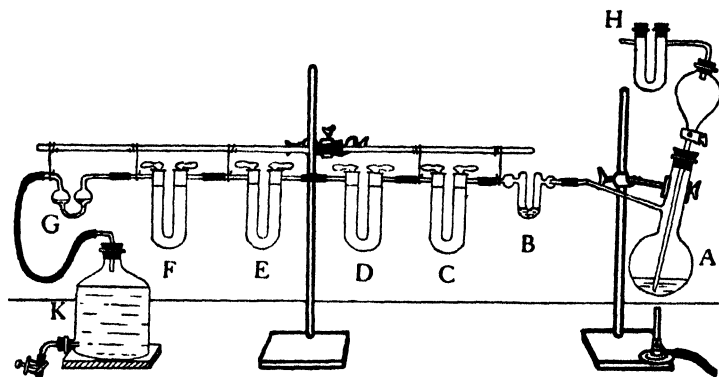



FIG. 61.

the latter should reach almost to the bottom of the flask, and the end should be drawn out to a point.

B. A U-tube, the open ends of which are sealed in the blowpipe flame, containing concentrated sulphuric acid. The acid is drawn in through one of the side-tubes, and the quantity is carefully adjusted until it is sufficient, *but no more than sufficient*, to seal the bend of the U-tube. The acid on the side-tube is volatilised by heating in a small flame.

C. A U-tube containing granulated pumice which has been soaked in concentrated copper sulphate solution, and afterwards heated for several hours in an air-oven at 160° in order partially to dehydrate the copper sulphate. The object of this tube is to retain hydrogen sulphide arising from decomposable sulphides present in the substance, and any hydrochloric acid that may be carried over with the carbon dioxide.

D. A U-tube containing moderately fine granular calcium chloride, free from powder. The calcium chloride is introduced through a cylinder of glazed paper, and the tube is filled to within 2 cm. of the side-tubes. Loose wads of glass wool are then placed in each limb, any calcium chloride adhering to the

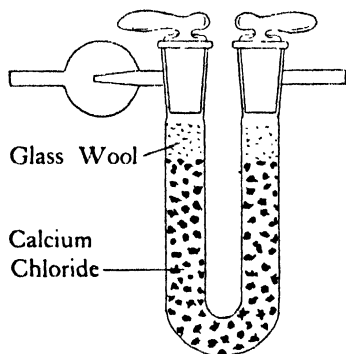
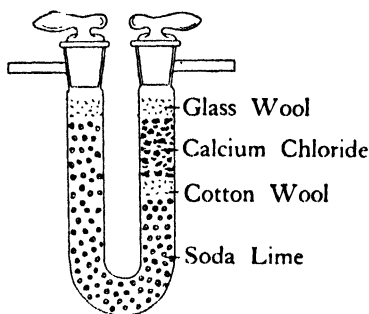



FIG. 62. FIG. 63.

upper part of the tube is removed, and the taps are made gas-tight with the minimum quantity of grease (Fig. 62).

In order to remove from the calcium chloride any free lime or basic chloride, which absorb carbon dioxide, a slow current of dry carbon dioxide (p. 476) is passed through the tube for five minutes in order to displace the air; the outlet tap of the U-tube is then closed, and the tube is left attached to the Kipp generator for several hours or overnight. The carbon dioxide in the tube is then displaced by passing dry air through it for about fifteen minutes.

E. and F. Two U-tubes containing soda-lime[1] and calcium chloride. A small wad of cotton-wool is placed near

[1] Soda-lime quickly deteriorates if exposed to the air, and soon becomes useless for the absorption of carbon dioxide. For this reason it is best to obtain it in *small*, well-corked bottles.

the middle of one limb, and fine granular soda-lime is introduced through a paper cylinder, so as to fill about three-fourths of the tube. The remaining fourth is filled with granular calcium chloride, and small wads of glass wool are placed in each limb (Fig. 63). The absorption of carbon dioxide by soda-lime takes place with evolution of heat, and loss of the water which is formed at the same time is prevented by the calcium chloride.

G. A pulsimeter and guard-tube, containing a few drops of concentrated sulphuric acid. The latter protects the calcium chloride in the last U-tube from atmospheric moisture, and also shows the rate at which air leaves the apparatus.

H. A tube containing soda-lime which removes carbon dioxide from the air that is finally drawn through the apparatus.

K. An aspirator; an inverted wash-bottle with the jet removed and supported on a retort-stand ring may be used. The flow of water is regulated by means of a screw-clip.

The best form of U-tube is provided with hollow, ground-in glass taps. If plain U-tubes are used, they may be closed with tightly-fitting rubber stoppers, or with ordinary well-softened corks, which are cut off flush with the top of the tube and made gas-tight by brushing over with melted paraffin wax.

The contents of the U-tubes must be protected from atmospheric moisture and carbon dioxide. This is accomplished with the first form of U-tube by simply turning the taps; plain U-tubes must be provided with caps, fitted over the side-tubes, and made from short pieces of rubber tubing closed with plugs of glass rod. The U-tubes are supported by wire hooks attached to a glass rod held in a clamp. They are connected with each other by means of short pieces of thick-walled rubber tubing (pressure tubing) which are lubricated by rubbing the inner surface with a little graphite, any excess of which is carefully removed.

Procedure.—Carefully wipe the two soda-lime absorption tubes and leave them in the balance-room for fifteen minutes before weighing. (Remove the rubber caps before weighing.)

In general, the amount of carbonate taken for analysis should be so chosen that the increase in weight of the soda-lime tube is about 0·3 gram.

Weigh the carbonate (*e.g.* about 1 gram of calcspar) in a

small tube, about 2·5 cm. long and 1·3 cm. wide. Place the tube and contents in the distilling flask, and moisten with a few drops of water.

Set up the apparatus as shown in Fig. 61. The U-tubes are attached one after the other beginning with B, and the ends of the glass tubes should be brought close together inside each rubber junction. The absorption tubes E and F must be so placed that *the limbs containing calcium chloride are turned towards the aspirator.* The aspirator is not connected at this stage.

Test the apparatus in order to find if it is gas-tight as follows :—Attach a piece of glass tubing to the guard-tube G, and dip the tube into a beaker of water. Open all the taps, apply gentle suction at H in order to lift a column of water in the tube attached to G, and then close the tap of the dropping-funnel. The apparatus may be considered gas-tight if the level of the water in the tube remains constant for several minutes.

Now place about 20 ml. of dilute hydrochloric [1] acid in the dropping-funnel, open the tap carefully, and regulate the flow of acid and the evolution of gas, so that about two bubbles per second pass through the acid in B.

After a slight excess of acid has been added, and when the evolution of gas has become slow, close the tap of the dropping-funnel and (by means of a pipette) remove any acid remaining in the latter. Warm the contents of the flask very gradually with a small flame until the liquid just boils. Boil gently for about one minute, then lower the flame until boiling just ceases, *and open the tap of the dropping-funnel.* Attach the aspirator and the soda-lime tube H, and draw a slow current of air through the apparatus. As soon as the first soda-lime tube becomes cold, extinguish the flame, and continue the current of air for fifteen minutes more.

Detach the soda-lime tubes and, after wiping them, leave them in the balance-room for about half an hour before weighing. The weight of the tube F should remain practically constant, any increase amounting to not more than about 1 mgrm. A decided increase in weight shows either that the experiment was conducted too hurriedly, or that the soda-lime is unsatisfactory.

[1] Perchloric acid may preferably be used instead of hydrochloric acid, as it is less volatile.

It is usual to calculate the percentage of carbonate in the substance as CO_2.

Indirect Method

OUTLINE OF METHOD.—A weighed quantity of the substance is decomposed by dilute acid in an apparatus of special design, and the loss in weight of the apparatus, due to the escape of carbon dioxide, is ascertained.

This method is not so accurate as the direct method (absorption by soda-lime), and its use is preferably restricted to the analysis of carbonates that can be decomposed by

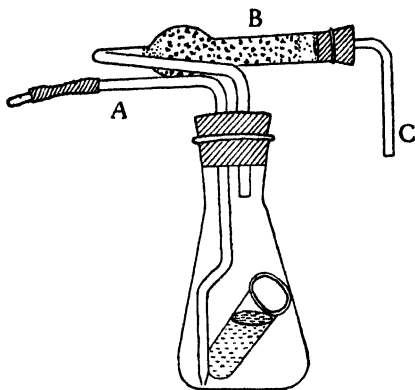



FIG. 64.

dilute *sulphuric* acid. If hydrochloric acid is used, its volatility makes it somewhat difficult to prevent loss of traces of that acid, and the result may be slightly high. In cases where an insoluble sulphate would be formed and sulphuric cannot be used, perchloric acid is preferable to hydrochloric acid as it is less volatile.

The Apparatus (Fig. 64) consists of a small, wide-mouthed flask (100 to 120 ml.), of thin glass for the sake of lightness. The flask is fitted with a rubber stopper, through which pass a calcium chloride drying-tube and a tube that reaches nearly to the bottom of the flask and is drawn to a point at its lower end. The drying-tube is filled with granular calcium chloride with glass-wool plugs at either end, and the calcium chloride must be saturated with carbon dioxide, as previously described (see the direct method). If the carbonate is to be decomposed by means of hydrochloric acid, one-third of the drying-tube B is

filled with granular pumice which has been soaked in concentrated copper sulphate solution and dried at 160°, and two-thirds with calcium chloride. The acid required for the decomposition of the carbonate is contained in a small test-tube, the length of which is so adjusted that the tube will stand obliquely in the flask, but cannot fall into a horizontal position. The tubes A and C are provided with rubber caps closed with short pieces of glass rod. Two additional straight calcium chloride tubes are also required.

Procedure.—Weigh the substance in the dry flask (*e.g.* about 2 grams of sodium carbonate crystals). Measure a slight excess of dilute sulphuric acid (5 to 10 ml.) or of 20 per cent. perchloric acid (10 to 15 ml.) into the small test-tube, and fit the apparatus together. Allow it to remain in the balance-room for fifteen minutes, remove the rubber caps, and weigh.

Replace the cap on the tube A, attach one of the supplementary calcium chloride tubes to C (in order to protect the contents of B from atmospheric moisture) and, by carefully tilting the flask, allow the acid, a few drops at a time, to come into contact with the carbonate. The evolution of carbon dioxide must not be rapid, otherwise moisture may be carried away with the gas. When the whole of the acid has been mixed with the carbonate and effervescence has ceased, warm the flask cautiously with a *very small* flame until the liquid is heated almost to the boiling-point. Then attach an aspirator [1] to C, and, the aspiration having been started, remove the cap on A, attach a calcium chloride tube to A, and draw a slow current of dry air through the apparatus for ten minutes. Remove the flame, continue the air current for ten minutes more, replace the caps on A and C, and, after an interval of about thirty minutes, weigh the apparatus (without the caps).

The loss in weight represents the carbon dioxide expelled from the carbonate.

CHLORATE

Chlorate is usually determined by reduction to chloride (p. 179) and determination of the chloride by one or other of the methods mentioned below.

[1] An evacuated Winchester quart bottle, closed with a rubber stopper through which passes a tube provided with a tap, makes a very convenient aspirator.

Volumetric methods for the determination of chlorate are described on pp. 149, 162, and 179.

CHLORIDE

Chloride may be determined volumetrically by the methods given on pp. 174 and 178.

The gravimetric determination of chloride is described on p. 230.

For methods of separately determining chloride, bromide, and iodide in mixtures, reference may be made to Treadwell's *Analytical Chemistry*, vol. 2. The following method for the determination of chloride and bromide in a mixture is an example of an indirect method of analysis.

Chloride and Bromide in a Mixture by Indirect Analysis

OUTLINE OF METHOD.—A measured volume of the solution is precipitated with excess of silver nitrate, the precipitate is collected on a sintered glass crucible and weighed. Another equal volume of the solution is similarly precipitated, filtered through a sintered glass crucible, and washed, but not dried. The precipitate is then treated with concentrated ammonia, which dissolves it in the moist condition. The solution formed is treated with excess of potassium bromide solution and then acidified. The precipitate, which now consists of silver bromide only, is collected in the same sintered glass crucible, dried and weighed. This type of indirect determination, though of theoretical interest, gives results which are seriously affected by small experimental errors; great care must therefore be taken in carrying out the work.

Make up 100 ml. of a solution of accurately known concentration of pure sodium chloride and potassium bromide, each salt being approximately decinormal. Measure out 10 ml. of this solution and precipitate it with silver nitrate as described on p. 230, wash by decantation, and finally on a weighed No. 3 sintered glass crucible. Dry at 150°, and weigh the silver chloride and bromide precipitate. As it is very difficult to dissolve the dried precipitate in ammonia, it is discarded, and the adhering particles are removed with a concentrated solution of sodium thiosulphate, and the crucible washed, dried, and weighed again. Precipitate another 10 ml. of the original solution, wash and filter it through the weighed crucible as before, and dissolve the moist precipitate in ammonia as

follows: Wash out the filter flask, and drain it as thoroughly as possible. Replace the adapter carrying the crucible, and close the side tube of the flask with a piece of rubber tube and screw clip, after introducing a very slight excess pressure with the mouth. Add about 10 ml. of concentrated ammonia, and stir the precipitate with a short glass rod, until this has practically all dissolved. It is not essential that it should dissove completely, provided the same crucible is used for the final precipitate, since the silver chloride will much more easily pass into solution than the silver bromide. Attach the filter flask to the pump, draw the solution through the crucible, and wash the latter five times with 2 ml. portions of dilute ammonia. Transfer the contents of the filter flask to the beaker in which the mixed silver halides were precipitated, and wash the flask first with a little dilute ammonia, then with water. To the solution in the beaker add 5 ml. of 10 per cent. potassium bromide, which will cause partial precipitation, then add dilute nitric acid until the solution is just acid. About 100 ml. of the acid will be required. Heat the solution to the boiling-point, allow it to cool, and after washing by decantation, collect the precipitate on the crucible in which the mixed silver halides were dissolved in ammonia. Wash the precipitate, dry at 150°, and weigh.

Let x and y respectively be the weights of NaCl and KBr in 10 ml. of solution, and w_1 and w_2 respectively the weights of AgCl+AgBr in the first precipitate, and the weight of AgBr in the second precipitate.

$$\frac{143\cdot3}{58\cdot45}x + \frac{187\cdot8}{119\cdot0}y = w_1$$

$$\frac{187\cdot8}{58\cdot45}x + \frac{187\cdot8}{119\cdot0}y = w_2$$

The values obtained for x and y should be compared with the weights of sodium chloride and potassium bromide used in making up the solution.

CHROMIUM

The volumetric method described on p. 133 is convenient and accurate.

In order to separate chromium from other metals, it is first

oxidised to chromate by fusion with sodium peroxide, or with a mixture of sodium carbonate and potassium nitrate; the chromate is determined volumetrically by the method already indicated, or gravimetrically as described below.

In the absence of all metals other than the alkalis, chromium may be determined by precipitation as hydroxide and conversion into oxide. The procedure is identical with that described under Aluminium on p. 229.

Chromic Hydroxide, when freshly precipitated, is a grey-green flocculent substance, insoluble in water. It is readily soluble in acids and in sodium hydroxide. It is sparingly soluble in ammonia, yielding a violet-red solution; on boiling this solution, the ammonia is expelled and the chromic hydroxide is precipitated. When dried at 100°, it loses water of hydration and becomes bluish-green. On ignition it is converted into chromic oxide, Cr_2O_3.

Chromic Oxide is a dark green powder which may be ignited strongly without loss of weight. The oxide, after strong ignition, is insoluble in hydrochloric acid.

CHROMATE AND DICHROMATE

Chromate and dichromate are usually determined volumetrically (p. 133). If the methods are practicable, the gravimetric determination as mercurous chromate or as barium chromate is easy and accurate. Chromate (or dichromate) may also be determined gravimetrically by reduction to a chromic salt, followed by precipitation as chromic hydroxide (see under Chromium).

Forms in which Chromate is precipitated

Mercurous Chromate.—The presence of chloride or sulphate, except in small amount, renders this method inaccurate.

Barium Chromate.—Chloride does not interfere with the use of this method, but sulphate must, of course, be absent. The properties of barium chromate and its precipitation are described on p. 283.

Determination of Chromate as Chromic Oxide after Precipitation as Mercurous Chromate

OUTLINE OF METHOD.—The chromate is precipitated as mercurous chromate, which on ignition is decomposed, leaving chromic oxide, Cr_2O_3.

Mercurous Chromate.—On addition of mercurous nitrate to a chromate, a brown precipitate of a basic salt separates. This quickly changes to the bright red, normal salt, Hg_2CrO_4. Mercurous chromate is insoluble in water and in very dilute nitric acid. On ignition, it is converted into chromic oxide (for the properties of chromic oxide, see p. 297). If the mercurous chromate is contaminated with much mercurous chloride, the precipitate is bulky and inconvenient, and chromic oxide is lost during the ignition.

Procedure.—Heat the neutral or slightly acid solution, and add mercurous nitrate until precipitation is complete. Keep the solution hot until the precipitate becomes bright red. Then add ammonia cautiously until a small quantity of a dark grey precipitate forms permanently. Heat until boiling, then cool, filter, and wash with a dilute mercurous nitrate solution. Dry the precipitate and the filter. Separate the precipitate and burn the filter before the addition of the precipitate. Ignite very gently at first and in a good draught, and finally ignite with the blowpipe. (**Caution.**—*The vapour given off during the ignition of the mercurous chromate is poisonous.*) Cool, and weigh the Cr_2O_3.

COBALT

Cobalt is determined after removal of metals precipitated by hydrogen sulphide in acid solution. From the analytical point of view, cobalt shows an extremely close relationship to nickel and, with one exception, the methods indicated on p. 325 for the determination of nickel may be used without modification for cobalt. Cobalt (unlike nickel) is not precipitated by dimethylglyoxime, and one of the best methods of separating cobalt from nickel is based on this fact (see p. 325); another method of separation is described below.

Forms in which Cobalt is precipitated

Cobalt Sulphide.—Precipitation with ammonium sulphide serves to separate cobalt, nickel, manganese, etc., from the alkalis and alkaline earths. Cobalt (and nickel) may be separated from manganese by precipitation with hydrogen sulphide in presence of acetic acid and ammonium acetate.

Cobaltic Hydroxide.—Cobaltic hydroxide is precipitated by bromine and sodium hydroxide, and the hydroxide is reduced to metallic cobalt, as described under Nickel (p. 326).

Cobalt Salt of Nitroso-β-naphthol.—This cobalt is insoluble in hydrochloric acid, whereas the corresponding nickel salt is soluble, and the method is very useful for the separation of a small quantity of cobalt from a comparatively large quantity of nickel.

Cobalt Oxinate.—By the use of this method cobalt may also be determined volumetrically.

Metallic Cobalt (Electrolytic).—The procedure is identical with that described for nickel on p. 248.

Determination of Cobalt by the Nitroso-β-naphthol Method

OUTLINE OF METHOD.—The cobalt is precipitated by means of nitroso-β-naphthol dissolved in acetic acid. The precipitate is washed, dried, and ignited. The cobalt oxide is either ignited in an atmosphere of hydrogen and the metallic cobalt weighed; or converted to sulphate.

Nitroso-β-naphthol, $C_{10}H_6 \cdot OH \cdot NO$, when pure, is a yellow, crystalline substance, insoluble in water. The reagent is a freshly prepared solution obtained by stirring 1 gram of the solid in 60 ml. of glacial acetic acid for several minutes, then adding 40 ml. of water, and filtering. The cobaltic compound, $(C_{10}H_6 \cdot O \cdot NO)_3Co$, is obtained as a voluminous, brick-red precipitate which is insoluble in dilute hydrochloric acid. The nickelous compound, $(C_{10}H_6 \cdot O \cdot NO)_2Ni$, is soluble in hydrochloric acid.

Procedure.—Dilute the solution, containing not more than 0·05 gram of cobalt as sulphate or chloride, to 150 ml. and add 5 ml. of concentrated hydrochloric acid. Heat to about 70° and add 25 to 50 ml. (according to the amount of cobalt) of the hot reagent. Allow the precipitate to settle, and ascertain whether precipitation is complete by adding more reagent to

the clear solution. Set aside for at least six hours. Filter through an 11-cm. paper. Wash the precipitate first with cold water, then with hot, dilute (4N) hydrochloric acid (in order to remove any nickel salt), and finally with hot water until free from acid. Dry the precipitate. Incinerate the paper together with the precipitate and about a decigram of pure oxalic acid (in order to facilitate removal of carbon) in a Rose crucible if the cobalt is to be weighed as metal; raise the temperature very cautiously, and ignite finally with a Méker burner. Reduce the cobalt oxide (mainly Co_3O_4) by heating in a current of hydrogen. Cool, and weigh the metallic cobalt.

A more convenient though less accurate method is to incinerate the precipitate with oxalic acid in an ordinary crucible until all the carbon is burnt off. Add 2 ml. of 2N sulphuric acid, and evaporate as far as possible on the water-bath. Place the crucible inside a larger iron crucible, the bottom of which has been covered with a thin pad of asbestos. Heat the outer crucible gradually to dull redness. Then cool, and weigh the cobalt sulphate, $CoSO_4$, which should not contain any black portions.

Determination of Cobalt as Oxinate

The use of oxine as a reagent is described under Aluminium (p. 278).

Procedure.—To the solution containing not more than 0·06 gram of cobalt add about 2 ml. of dilute hydrochloric acid and 25 ml. of 2N ammonium acetate. The final volume of the solution should be about 60 ml. Warm to about 60°, and run in from a burette 1 ml. of the oxine solution, prepared as described on p. 278, for every 3 mgrm. of cobalt present. After mixing, the solution should have a yellow colour showing the presence of excess of the reagent. Heat nearly to boiling, filter through a No. 3 sintered glass crucible, wash with hot water, or, better, with a hot saturated solution of cobalt oxinate, dry at 150°, and weigh as $Co(OC_9H_6N)_2$.

Instead of drying and weighing the precipitate, it may be dissolved in warm 6N hydrochloric acid and aliquot parts titrated with a standard bromate-bromide mixture as described under Aluminium (p. 279). The volume of oxinate solution taken for titration should not contain more than 0·015 gram

of cobalt. One ml. of the standard bromate solution is equivalent to 0·737 mgrm. of cobalt.

COPPER

Copper may be determined volumetrically (see p. 143). In gravimetric analysis, copper is precipitated in acid solution, together with many other metals, by hydrogen sulphide.

A colorimetric method for the determination of traces of copper is described on p. 261.

Forms in which Copper is precipitated

Cupric Oxide.—This is a convenient and accurate method, but is seldom applicable, as other metals that give insoluble oxides may be present. For details, see p. 231.

Cuprous Thiocyanate.—Since most thiocyanates are soluble, this method is sometimes useful for the separation of copper from other metals. Lead, mercury, and silver interfere, their thiocyanates being also insoluble. The cuprous thiocyanate may either be weighed as described below, or estimated volumetrically (see p. 168).

Cupric Thiocyanate and Pyridine Complex. — This method obviates any necessity to reduce the copper to the cuprous state.

Metallic Copper (Electrolytic method).—This is probably the best method for separating copper from the other metals precipitated with it by hydrogen sulphide in acid solution. For details, see pp. 245 and 246.

Determination of Copper as Cuprous Thiocyanate

OUTLINE OF METHOD.—The copper is precipitated with ammonium thiocyanate in presence of sulphurous acid, and is weighed as cuprous thiocyanate.

Cuprous Thiocyanate, $Cu_2(CNS)_2$, is a pure white, crystalline precipitate, almost insoluble in water and in dilute hydrochloric, sulphuric, and sulphurous acids. It may be dried without decomposition at temperatures not exceeding 150°.

The solution for analysis should be made *slightly* acid

with sulphuric acid. Nitrates or other oxidising agents, if present, must be removed by evaporation with sulphuric acid.

Procedure.—Weigh out accurately about 0·5 gram of copper sulphate, $CuSO_4, 5H_2O$, and dissolve it in about 100 ml. of water. Add 3 grams of sodium bisulphite, and 20 ml. of dilute sulphuric acid; or, preferably, add 5 ml. of dilute sulphuric acid, and excess of sulphurous acid. Then to the cold solution add ammonium thiocyanate drop by drop with constant stirring until all trace of blue colour has disappeared, carefully avoiding much excess. When the precipitate has settled (which may be after some hours), filter through a Gooch or fine sintered glass crucible, and wash with cold water until ferric chloride gives no coloration with the washings. Wash finally several times with 20 per cent. alcohol, dry at a temperature not exceeding 150°, and weigh as $Cu_2(CNS)_2$. As an alternative, the precipitate may be estimated by titration with potassium iodate in the presence of a sufficient concentration of hydrochloric acid (see p. 168).

Determination of Copper as Cupric Thiocyanate and Pyridine Complex

Copper may be determined rapidly, in the absence of metals other than those of the alkali and alkaline earth groups, and magnesium, by means of the complex formed between its thiocyanate and pyridine, $Cu(CNS)_2,(C_5H_5N)_2$. (Spacu and Dick, *Z. Anal. Chem.*, 1927, vol. 71, p. 185.) This compound is slightly soluble in pure water, and more soluble in acetone, but it is almost insoluble in absolute alcohol and ether. It is stable at temperatures below 60°.

Procedure.—Weigh out accurately between 0·3 and 0·4 gram of copper sulphate, and dissolve in 100 ml. of water in a 250 ml. beaker. Add slowly from a pipette, while stirring, about 2 ml. of pyridine, and then 0·5 gram of ammonium thiocyanate, or 70 ml. of a decinormal solution of this salt. Allow the precipitate to settle, and decant the greater portion of the liquid through a weighed Gooch or fine sintered glass crucible. Transfer the precipitate with the remainder of the liquid to the crucible, and wash the beaker and precipitate with water containing 0·3 per cent. of pyridine and ammonium thiocyanate; or, preferably, with water which has been

saturated by shaking with a portion of the precipitate previously prepared. Complete the washing with two or three portions of absolute alcohol, followed by ether, each containing a trace of pyridine. Acetone must not be used. Dry in a vacuum until the weight is constant. The drying can be accelerated by previously warming for a short time in an air-oven not above 45°.

FLUORIDE

Both gravimetric and volumetric methods are used for the determination of fluoride. Gravimetrically, fluoride is usually precipitated and weighed as calcium fluoride. One of the simplest methods of determining fluorine in fluorides, or in silicates decomposable by sulphuric acid, is to expel the fluorine as silicon fluoride and measure the volume of the gas. A full description of various methods of determination is given in Mellor's *Quantitative Inorganic Analysis*, and in Hillebrand and Lundell's *Applied Inorganic Analysis*.

A volumetric method for the determination of fluoride is given on p. 186.

Determination of Fluoride in a Silicate Rock

OUTLINE OF METHOD.—The powdered substance is fused with sodium carbonate and the resulting mass extracted with water and filtered. After removal of the silica and bases from the solution by means of ammonium carbonate, calcium chloride is added, and the precipitated calcium fluoride and calcium carbonate is ignited, The calcium carbonate is removed with acetic acid, and the residual calcium fluoride is ignited and weighed.

Calcium Fluoride is a white, gelatinous precipitate, sparingly soluble in hydrochloric and nitric acids, and nearly insoluble in acetic acid. It is more soluble in presence of ammonium salts. The precipitate is very difficult to filter, but if precipitated together with some calcium carbonate the filtration is much easier. Calcium fluoride cannot be completely decomposed by fusion with sodium carbonate unless it is mixed with silica or a silicate.

Procedure.—Weigh accurately in a platinum crucible about 2 grams of the rock powder and mix it with 12 grams of dry sodium carbonate. (In the case of a fluoride containing but little silica, 4 grams of silicic acid must also be added.) Heat

the mixture gradually to redness, and maintain the temperature until effervescence ceases (*cf.* p. 341). Do not use the blowpipe. After cooling, place the crucible in a large porcelain basin or casserole, and extract the mass thoroughly with hot water, taking care to break down any large lumps. Filter, and wash with hot water. The filtrate contains all the fluoride.

Add about 10 grams of ammonium carbonate and set aside for about twelve hours in a warm place. Filter the precipitated silica and alumina, and wash with dilute ammonium carbonate solution. Heat the covered beaker containing the filtrate on the steam-bath until the ammonium carbonate is decomposed and the evolution of carbon dioxide ceases. In order to remove the last traces of silica, add about 5 ml. of a solution of precipitated zinc oxide in 10 per cent. ammonia, and evaporate until the smell of ammonia disappears. Filter, and wash with water.

Add dilute nitric acid to the filtrate until the alkali carbonate is nearly, but not entirely, decomposed. If too much acid is added, make the solution alkaline again with sodium carbonate. Then add excess of calcium chloride, and heat until boiling. Filter the precipitated calcium fluoride and calcium carbonate on ashless paper pulp, wash with hot water, dry, and ignite at a low red heat in a platinum crucible. After cooling, add sufficient acetic acid to dissolve the calcium carbonate and oxide; warm the covered crucible on the steam-bath until effervescence ceases, and then evaporate to dryness. Extract with hot water containing a few drops of acetic acid, filter, wash, and ignite the residue. Repeat the extraction with very dilute acetic acid, and finally ignite to faint redness and weigh the CaF_2.

It is advisable to check the result by converting the calcium fluoride into calcium sulphate. Add a few drops of concentrated sulphuric acid and evaporate carefully (Fig. 13, p. 29, or Fig. 42, p. 213). Ignite at a low red heat, and weigh the $CaSO_4$.

GOLD

OUTLINE OF METHOD.—Gold is determined by reduction of its compounds by means of hydroquinone, the resulting metal being weighed.

Ferrous sulphate, sulphur dioxide, and oxalic acid are often used as reducing agents, but hydroquinone has advantages over these. The use of ferrous sulphate involves the subsequent

separation of iron from the platinum metals if these are present; sulphur dioxide tends to bring down platinum together with the gold; and oxalic acid is slow in reduction, and the fine state of division of the gold makes filtration difficult.

Precipitation is carried out in hydrochloric acid of rather more than normal concentration, under which conditions the platinum metals, even if present in amounts double that of the gold, are not precipitated. The gold is also separated from such common metals as copper, zinc, and nickel, though the action of the reducing agent should not be prolonged beyond the period indicated in any determination. Tungsten interferes and must be removed if present.

Procedure.—If aqua regia has been used to dissolve the metal, evaporate the resulting solution three times with small amounts of concentrated hydrochloric acid, after the addition of a little sodium chloride, to remove excess of nitric acid. Dissolve the residue in 15 ml. of water, and 8 ml. of concentrated hydrochloric acid. Filter the solution through a small filter, wash, and dilute the solution to about 50 ml. The amount of gold present should be not more than 0·1 gram.

If the gold to be determined is already present in solution as chloride, a volume containing not more than 0·1 gram of gold is taken, 8 ml. of concentrated hydrochloric acid is added, and the mixture adjusted to about 50 ml.

Heat the prepared solution, and add a freshly prepared 1 per cent. aqueous solution of hydroquinone from a dropping-funnel (p. 236), using 30 ml. of the reagent, while stirring continuously. Boil the mixture gently for fifteen minutes, and filter through a small paper filter, neglecting any brown colour in the filtrate. Wash repeatedly with hot water, dry, ignite in a *porcelain* crucible, and weigh.

HYDRAZINE—HYDROXYLAMINE

Volumetric methods for the determination of these compounds are described on pp. 165-166.

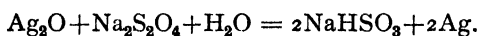
HYPOCHLORITE

The only common hypochlorites are those of calcium and sodium. Volumetric methods are described on pp. 151 and 159, and a gas-volumetric method on p. 434.

HYPOSULPHITE (DITHIONITE)

OUTLINE OF METHOD.—A weighed amount of sodium hyposulphite is added to an excess of silver oxide dissolved in ammonia (thus avoiding air oxidation) whereby an equivalent quantity of the silver complex is reduced. The silver deposited is weighed in a sintered glass crucible after washing and drying. Alternately the silver may be dissolved in nitric acid and the silver nitrate titrated with standard thiocyanate.

Sodium hyposulphite is a strong reducing agent, and it should be exposed as little as possible to atmospheric oxygen. It reacts with silver oxide dissolved in ammonia according to the following equation :—

$$Ag_2O + Na_2S_2O_4 + H_2O = 2NaHSO_3 + 2Ag.$$

Procedure.—Add dilute ammonia to about 70 ml. of approximately decinormal silver nitrate in a beaker, until the precipitate of silver oxide first formed is redissolved, and then add an excess of about 5 ml. of ammonia. Place about 1 gram of sodium hyposulphite in a stoppered weighing bottle and weigh it accurately. Transfer about 0·3 gram directly into the beaker containing the ammoniacal silver solution while stirring continuously. Reweigh the weighing bottle, to determine the amount of solid transferred. Pour the supernatant liquid through a weighed No. 3 sintered glass filter, using only gentle suction to avoid drawing through any of the finely divided silver which remains suspended in the solution. Wash by decantation three or four times with distilled water, and transfer the silver to the filter and wash it until a little of the filtrate collected separately gives no precipitate with hydrochloric acid. Dry the crucible at 130°, and weigh.

Instead of weighing the silver it may be dissolved in nitric acid and titrated with standard thiocyanate solution. This can be done by washing out the filter flask, adding a hot mixture of 5 ml. of concentrated nitric acid and 5 ml. of water to the crucible and covering it with a watch-glass. When the action of the acid has ceased, draw the solution through into the flask (avoiding any contact with rubber). Repeat the treatment with hot acid and water, and finally wash the crucible thoroughly with distilled water. Transfer the filtrate to the beaker in which the silver was precipitated, boil to remove oxides of nitrogen, and cool. Titrate the silver nitrate with standard thiocyanate solution as described on p. 176.

IODIDE

Iodide is readily determined by the volumetric methods described on pp. 136, 167, 174 and 178.

It may also be determined gravimetrically by precipitation as silver iodide. The procedure is identical with that given for the determination of chloride (p. 230), except that there is no need to protect the precipitate from light.

Silver iodide is much less soluble in almost all solvents than either the chloride or bromide. The solubility in water is negligibly small (0·003 mgrm. per litre at 20°). It is practically insoluble in dilute nitric acid and very sparingly soluble in ammonia (35 mgrms. per litre in 10 per cent. ammonia at 15°). It is appreciably soluble in concentrated silver nitrate and other salt solutions. Silver iodide fuses, without decomposition, at 552°.

IRON

On account of its rapidity and accuracy, a volumetric determination of iron (see Index) is preferable to any gravimetric method.

A volumetric method may often be applied after the iron has been separated gravimetrically from most other metals, and it is one of the best methods for the determination of the iron in a mixed precipitate of ferric and aluminium oxides (compare pp. 382 and 387).

In gravimetric analysis, iron is always determined after removal of the metals precipitated by hydrogen sulphide in acid solution. It is sometimes precipitated, together with aluminium, chromium, titanium, manganese, nickel, cobalt, and zinc, by ammonium sulphide, and is then separated from the other metals. In absence of the other metals of this group, it is preferable to precipitate iron and aluminium as hydroxides with ammonia.

The separation of iron from manganese, etc., is a matter of some difficulty. The " cupferron " method, described below, is easier, more rapid, and no less accurate than the older basic acetate method.

A colorimetric method for the determination of traces of iron is described on p. 256.

Forms in which Iron is precipitated

If not already in the ferric state, the iron is always oxidised before precipitation, ferrous hydroxide being slightly soluble.

Ferric Hydroxide.—This is the easiest gravimetric method for the determination of iron, but is of limited applicability. For details, see p. 225.

Basic Ferric Acetate.—This method provides a separation from manganese, chromium, zinc, nickel, and cobalt, but aluminium is precipitated with the iron. For details, see under Aluminium, p. 275.

Ferric Salt of Nitrosophenyl Hydroxylamine ("Cupferron" Method).—Iron is precipitated by "cupferron" from strongly acid solutions. This method provides a complete separation of iron from all metals other than the silver and copper groups, and is particularly useful for the separation of iron from aluminium, manganese, and chromium.

Determination of Iron by the "Cupferron" Method

OUTLINE OF METHOD.—The iron (in the ferric state) is precipitated from a strongly acid solution by "cupferron," and the precipitate is converted into ferric oxide by ignition.

Cupferron is the ammonium salt of nitrosophenyl hydroxylamine, $C_6H_5N(NO)ONH_4$. It precipitates most of the heavy metals from neutral solutions as insoluble salts. From strongly acid solutions, however, only the cupric and ferric compounds are precipitated. The method is therefore useful for the separation of iron from manganese, aluminium, etc. The separation is remarkably complete, but in cases where large amounts of aluminium, manganese, or chromium are present, a second precipitation is advisable.

The precipitate of the ferric salt is rather bulky, and the amount of material taken should therefore be such as to yield about 0·1 gram of ferric oxide. The solubility of the precipitate appears to be negligible, even in 4N hydrochloric acid.

Procedure.—To the solution add 20 ml. of concentrated hydrochloric acid and dilute to 100 ml. Dissolve about 3 grams of cupferron in 50 ml. of cold water, and add it slowly and with constant stirring to the ferric salt solution. A brownish-red precipitate, which is partly crystalline and partly amorphous,

separates. Excess of cupferron is shown by the formation of a white precipitate in the supernatant liquid. Stir well, but do not heat the solution.

Filter with suction. If the precipitate adheres tenaciously to the beaker, dissolve it in a little ether and then remove the ether by addition of a little boiling water.

Wash with cold water until almost free from acid, then twice with diluted (6N) ammonia, and finally twice with water. Place the wet paper and precipitate in a porcelain crucible and heat gently until no more inflammable gases are given off. Ignite, and weigh the ferric oxide obtained.

Exercise.—Determine the percentage of iron in ferric alum.

LEAD

In the analysis of a mixture, lead is usually determined as sulphate, although the chromate method is preferable if it can be used. The separation of lead from calcium by precipitation as sulphide is described in connection with the analysis of glass (p. 391).

A colorimetric method for the determination of traces of lead is described on p. 262.

Forms in which Lead is precipitated

Lead Sulphate.—This method provides a separation from all metals except barium, strontium, calcium, and mercury.

Lead Chromate.—This method is more accurate than the sulphate method, but is limited in applicability on account of the general insolubility of chromates.

Lead Peroxide (Electrolytic).—Lead may be separated from almost all other metals by this method. For details, see p. 250.

Determination of Lead as Sulphate

OUTLINE OF METHOD.—The solution is evaporated with concentrated sulphuric acid until all hydrochloric or nitric acid is expelled. After dilution, the lead sulphate is filtered, washed with alcohol, dried, and weighed as $PbSO_4$.

Lead Sulphate is a heavy, white powder which is sparingly soluble in water. One litre of water at 18° dissolves about 40 mgrms. of the salt. It is much less soluble in dilute sulphuric

acid, but with increasing concentration of sulphuric acid the solubility again increases. It is readily soluble in hot concentrated hydrochloric and nitric acids. It is soluble in solutions of almost all ammonium salts and in solutions of alkali hydroxides, but is almost insoluble in alcohol. It may be heated to a bright red heat without decomposition if reducing gases are excluded from the crucible. At a red heat, it is readily reduced by carbonaceous matter, with loss of lead by volatilisation.

Procedure.—To the lead solution add 3 ml. of concentrated sulphuric acid, and evaporate in a porcelain basin on the steam-bath and then over a Rose burner until dense white fumes are evolved. Cool, dilute to about 100 ml. with cold water, and stir. The precipitate may be filtered more readily if it is kept for a few hours before filtration.

Filter through a Gooch or sintered glass crucible. Wash the precipitate several times with the minimum quantity of N sulphuric acid, and finally with alcohol.

Dry at 100°, place the crucible inside a nickel crucible, and heat until of constant weight.

Determination of Lead as Chromate

OUTLINE OF METHOD.—The lead is precipitated as chromate by the addition of potassium chromate (or dichromate). The precipitate is collected in a Gooch or sintered glass crucible, dried at 120°, and weighed as $PbCrO_4$.

Lead Chromate is almost insoluble in water and in acetic acid (1 litre of water dissolves 0·1 mgrm. at 18°), slightly soluble in nitric acid, and readily soluble in alkali solutions. It may be dried completely at 120°, but loses oxygen if heated to its melting-point.

Procedure.—If the solution is neutral or alkaline, add acetic acid until it is distinctly acid. If the solution contains nitric acid, add sufficient sodium acetate (5 to 10 grams) to replace the nitric acid by acetic acid. To the hot solution add potassium chromate (2 per cent. solution) in slight excess. Place the beaker on the steam-bath until the precipitate settles. Examine the supernatant liquid, which must be coloured slightly yellow. Filter through a Gooch or sintered glass crucible, wash thoroughly with hot water, and dry at 120°.

LITHIUM (POTASSIUM AND SODIUM)

Lithium, potassium, and sodium often occur together, and if the material to be analysed contains the three metals, they are first separated from all other metals. They are then converted to chlorides, made completely anhydrous, and ammonium salts (if present) driven off by volatilisation. Lithium chloride is extracted by means of a suitable organic solvent, leaving the sodium and potassium chlorides undissolved. The lithium in the extract is finally weighed as sulphate.

Whilst the potassium and sodium in the residue may be determined by a direct method, as described under these metals, the amount of each present may also be found by weighing the two chlorides together, and determining either one of the metals or the total chloride present, and calculating the weights of the two metals from the data obtained.

The preliminary extraction of lithium, sodium, and potassium in an insoluble silicate is described on p. 388.

Treatment of the Solution for Analysis

If the metals other than the alkali metals and acid radicals other than chlorides are present, the following treatment must be carried out. Evaporate the solution with a slight excess of sulphuric acid, and heat carefully until thick white fumes are evolved. Cool, dilute, and to the hot solution add a slight excess of barium chloride solution. Boil for a few minutes, cool slightly, and without filtering make the solution alkaline with ammonium hydroxide. Add ammonium carbonate solution in sufficient amount to precipitate the excess of barium and other metallic radicals. Boil, wash by decantation, and filter. Wash the residue until all chlorides are extracted. Evaporate the filtrate to dryness, and gently ignite to remove ammonium salts, avoiding fusion in the process, and observing the precautions described on p. 339, under the determination of sodium and potassium. Dissolve the residue, and precipitate traces of barium (and calcium) still present by the addition of a few drops of ammonium hydroxide, ammonium carbonate, and ammonium oxalate. Filter through a small filter, wash, evaporate, and again gently ignite.

The lithium chloride must now be separated from the potassium and sodium chlorides in the following manner.

Determination of Lithium in the presence of Sodium and Potassium

OUTLINE OF METHOD.—All metals other than lithium, sodium, and potassium, and all acid radicals other than chloride having been removed as described above, the completely anhydrous solid is extracted with anhydrous acetone, which dissolves out the lithium chloride alone. *Lithium Chloride* is soluble in many organic liquids in which the chlorides of the other alkali metals are inappreciably soluble. Such solvents are amyl alcohol, isobutyl alcohol, acetone, and dioxan. Of these acetone is the most convenient. Dioxan (recently suggested) is liable to peroxidation and may give rise to dangerous explosions on distillation. Lithium chloride fuses at 606°, and volatilises at this temperature.

Procedure.—Dissolve the solid containing only the chlorides of lithium, sodium, and potassium in the least possible amount of water in a porcelain crucible (or small dish) which has been previously weighed with a watch-glass cover. Add 5 to 10 drops of concentrated hydrochloric acid to convert any lithium hydroxide present to chloride. Evaporate as far as possible on a water-bath, cover the crucible with the watch-glass, and heat in an air-oven at 160° for an hour.

In the meanwhile, support a coarse grain sintered glass crucible (Nos. 1 or 2) just below the top of a wide-mouthed 250 ml. flask, using either platinum wire or thread which has been previously extracted with acetone. The wire or thread may be conveniently held in position by a rubber band round the outside of the flask. Bore a cork to carry a small reflux condenser and extract the cork with acetone to remove soluble matter.

After cooling the crucible containing the chlorides in a desiccator, rapidly weigh it covered with the watch-glass, and immediately after weighing transfer as much as possible of the solid to the sintered glass crucible in the extraction flask. This can be done with the aid of a short piece (5 cm.) of glass rod flattened at the end, and a jet of anhydrous acetone from a small wash-bottle. The glass rod is then left inside the sintered glass crucible, and the reflux condenser is attached to the flask. Add more anhydrous acetone through the condenser until about 50 ml. is present. Heat on the water-bath for three hours, regulating the flame so that the solid in the crucible is covered throughout by the condensed acetone. Meanwhile gently ignite the crucible from which most of the mixed

chlorides were transferred, cool and weigh it with the watch-glass. From the loss in weight the proportion of the original mixed chlorides transferred may be calculated and an allowance made for the small amount which remains behind.

After the extraction is finished, cool and remove the crucible containing the residue of sodium and potassium chlorides, which may be determined if desired as described on p. 338. Distil off the acetone in the flask, and determine the lithium either by titrating a suitable portion with standard silver nitrate, or by converting it to lithium sulphate as described below.

Determination of Lithium as Lithium Sulphate

OUTLINE OF METHOD.—A slight excess of sulphuric acid is added to the lithium salt solution in a small dish. The mixture is evaporated to dryness, and ignited to lithium sulphate, Li_2SO_4. Other metals, and acid radicals not converted to sulphate by this treatment must be absent.

Lithium Sulphate is more easily obtained free from the bisulphate by ignition than is the case with the other alkali metals. It is therefore unnecessary to add ammonium carbonate for the final ignition. The sulphate is not volatile at a dull red heat.

Procedure.—Weigh out accurately about 0·3 gram of lithium chloride in a stoppered weighing bottle, the salt being very hygroscopic. Transfer the contents to a small weighed dish, preferably of platinum, using as little water as possible. Add 0·5 ml. of concentrated sulphuric acid to the solution, and evaporate to dryness on the water-bath. Heat with a very small flame until no further evolution of white fumes is noticed; then raise the temperature to a dull red heat, maintaining this for about fifteen minutes, cool, and weigh. Repeat the ignition until the weight is constant.

MAGNESIUM

On account of their alkaline character, magnesium carbonate and hydroxide may be determined volumetrically.

Forms in which Magnesium is precipitated

Magnesium Ammonium Phosphate.—This is the method in common use. The process takes considerable time, and to obtain correct results, the conditions of procedure laid down must be carefully observed.

In the analysis of a mixture by this method, metals belonging to the copper, iron, zinc, and calcium groups must first be removed. A typical example of the separation of magnesium from calcium and other metals is described on p. 380.

Magnesium Oxinate.—By the use of this method the preliminary separation of calcium is avoided.

Determination of Magnesium as Pyrophosphate after Precipitation as Magnesium Ammonium Phosphate

OUTLINE OF METHOD.—The magnesium is precipitated as magnesium ammonium phosphate by means of ammonium hydrogen phosphate and ammonia. The precipitate is either converted into magnesium pyrophosphate by ignition, and weighed as $Mg_2P_2O_7$; or it may be weighed directly as the hexahydrate of magnesium ammonium phosphate.

Magnesium Ammonium Phosphate, $MgNH_4PO_4, 6H_2O$, is a white, crystalline substance which is somewhat soluble in water. At the ordinary temperature, 1 litre of water dissolves about 65 mgrms. It is much less soluble in ammonia.

In order to obtain a precipitate of normal composition ($MgNH_4PO_4$), the solution must be just acid until after the phosphate solution has been added; and the ammonia must be added last. If the precipitation takes place in the presence of much ammonium salt, the precipitate contains $Mg_3(PO_4)_2$, or $Mg(NH_4)_4(PO_4)_2$; the former is unchanged by ignition, and the latter gives magnesium metaphosphate, whereas the precipitate of normal composition is converted into magnesium pyrophosphate.

If the precipitation takes place in the presence of much potassium or sodium salt, the precipitate is contaminated with magnesium potassium (or sodium) phosphate. So that if much ammonium, potassium, or sodium salt is present, reprecipitation is essential. In any case, reprecipitation is desirable to procure the best results.

On heating to 100°, magnesium ammonium phosphate loses 5 molecules of water; above 200°, it is converted into magnesium pyrophosphate.

Magnesium Pyrophosphate, $Mg_2P_2O_7$, is unchanged by ignition in air, but if ignited in contact with carbon above 900°, phosphorus is lost. Magnesium pyrophosphate melts at about 1220°.

Exercise.—Weigh accurately about 0·5 gram of magnesium sulphate, $MgSO_4,7H_2O$, and transfer to a 350 ml. beaker. Dissolve in water, and determine the magnesium as follows.

Procedure.—The following method is based on the procedure recommended by Epperson (*J. Amer. C. S.*, 1928, vol. 50, p. 321), and modified by Hoffman and Lundell (*Bureau of Standards, J. Res.*, 1930, vol. 5, p. 279).

To the solution of magnesium sulphate, containing not more than 0·1 gram of magnesium oxide, add 5 to 10 ml. of concentrated hydrochloric acid, and dilute to a volume of 125 to 150 ml. Add 1 ml. of methyl red, cool well, and add 10 ml. of a freshly prepared solution of diammonium hydrogen phosphate containing 25 grams of this salt to 100 ml. of water. Neutralise, while stirring, with ammonia (0·9 sp. gr., *i.e.* about 80 ml. of 0·880 ammonia made up to 100 ml. with water) added from a burette. Stir for five minutes, then add 5 ml. more of the ammonia solution, and stir for ten minutes. After standing for four hours, or preferably overnight, filter through close texture paper, and wash the precipitate two or three times with a solution of ammonia (5 ml. of 0·880 ammonia diluted to 100 ml.). Dissolve the precipitate on the filter with about 50 ml. of warm normal hydrochloric acid, and wash the paper thoroughly with hot very dilute (1 in 100) hydrochloric acid. Add methyl red, and about 1 ml. of the above ammonium phosphate solution. Complete the precipitation as before. The final volume should be between 100 and 150 ml. Allow to stand at least four hours.

(1) *If the precipitate is to be converted into the pyrophosphate for weighing*, filter and wash the precipitate with ammonia diluted as above until a few drops of the filtrate give no turbidity with dilute nitric acid and silver nitrate. Dry the filter with the precipitate in the steam-oven, and incinerate the paper, apart from the precipitate, *at as low a temperature as possible* in the manner described on p. 219, using preferably a platinum crucible. If the paper is moistened with dilute ammonium nitrate, a white ash is more easily obtained eventually. The paper should not be allowed to take fire. After all volatile carbonaceous matter has been driven off, the residue may be ignited strongly with the lid open enough to allow circulation of air, until the residue is as white as possible. Add the precipitate, and ignite to constant weight at a temperature not

exceeding 1100°. If a platinum crucible is being used, a good Bunsen flame will be adequate, but for a porcelain crucible the blowpipe is permissible.

From the weight of magnesium pyrophosphate obtained calculate the percentage of magnesium in magnesium sulphate.

(2) *If the precipitate is to be weighed as the hexahydrate of magnesium ammonium phosphate*, filter through a Gooch or sintered glass crucible, and wash with ammonia diluted as above until a few drops of the filtrate give no turbidity with dilute nitric acid and silver nitrate. Wash finally either with three small portions of alcohol followed by similar treatment with ether, or with five small portions of acetone. In either case the crucible is then placed in an oven at 30° to 35° for a quarter of an hour, cooled, and weighed as $MgNH_4PO_4,6H_2O$.

Determination of Magnesium by means of Oxine

The use of this reagent has been described under Aluminium (p. 278), and it may be conveniently employed in the determination of magnesium.

Procedure.—Weigh out accurately an amount of magnesium sulphate containing not more than 0·04 gram of magnesium. Dissolve this in about 100 ml. of water in a 250 ml. beaker. Add 5 ml. of ammonium chloride solution, and add dilute ammonia until the liquid is just alkaline. Heat to about 70°, and run in from a burette a solution of oxine prepared by warming 2 grams of oxine with 6 ml. of glacial acetic acid and 10 ml. of water, and finally diluting to 100 ml. One ml. of this solution must be added for every 1·5 mgrm. of magnesium present, a large excess being avoided as some of the reagent might be precipitated with the magnesium oxinate. Add 3 ml. of concentrated ammonia, and stir thoroughly. After the precipitate has settled, the supernatant liquid will be yellow in colour, indicating the presence of oxine in excess. Allow the mixture to cool, filter through a Gooch or sintered glass crucible, and wash the precipitate thoroughly with hot water containing a little ammonia. Dry at 105°, and weigh as $Mg(OC_9H_6N)_2,2H_2O$; or at 150° to 160°, and weigh as $Mg(OC_9H_6N)_2$.

Instead of drying and weighing the precipitate, it may be dissolved in warm 2N hydrochloric acid and titrated with a

bromate-bromide mixture as described under Aluminium (p. 279). In this case the volume of oxinate solution taken for titration should not contain more than 0·01 gram of magnesium. One ml. of the standard bromate solution is equivalent to 0·304 mgrm. of magnesium.

MANGANESE

Manganese may be determined volumetrically (p. 112).

In gravimetric analysis, manganese is always determined after removal of the metals precipitated in acid solution by hydrogen sulphide. Hillebrand, in his *Analysis of Silicate and Carbonate Rocks*, states that "the gravimetric determination of manganese in small amount seems to be more of a stumbling-block to the average chemist than that of almost any other of the frequently occurring elements in mineral analysis. This is due almost always to incomplete prior precipitation of elements which later suffer co-precipitation with the manganese."

A colorimetric method for the determination of traces of manganese is described on p. 264.

Forms in which Manganese is precipitated

Manganous Carbonate.—This method is applicable in the absence of other metals that form insoluble carbonates. Only the alkalis and ammonium salts may be present.

Manganese Dioxide (Hydrated).—Precipitation in this form by means of ammonium persulphate provides a method of separation from chromium. If more than traces of zinc, nickel, or cobalt are present, a second precipitation is necessary for complete separation.

Manganese Sulphide.—In this form, manganese is precipitated by means of ammonium sulphide along with nickel and cobalt. The nickel and cobalt are removed by precipitation with hydrogen sulphide in presence of acetic acid and ammonium acetate.

Manganese Ammonium Phosphate.—On account of the general insolubility of phosphates, this method is of limited applicability, but the precipitate obtained is so easily filtered that the method has marked advantages when no separation

from other metals is required. The procedure is identical with that described for zinc in presence of alkalis (p. 360). Ammonium chloride is added prior to the precipitation, and the precipitate is converted into the pyrophosphate, $Mn_2P_2O_7$, by gentle ignition.

Determination of Manganese as Oxide after Precipitation as Carbonate

OUTLINE OF METHOD.—The manganese is precipitated as manganous carbonate by means of ammonium carbonate. By ignition, first in air and then in a current of carbon dioxide, the precipitate is converted into Mn_3O_4, which is weighed ; or it may be converted into and weighed in one or other of the forms mentioned below.

Manganous Carbonate is a buff-coloured powder which darkens somewhat on exposure to air and is sometimes difficult to filter. It is practically insoluble in water and in solutions of ammonium salts. It dissolves in acids and is slightly soluble in solutions of alkali carbonates.

At a high temperature, with access of air, manganous carbonate is converted mainly into Mn_3O_4, together with traces of Mn_2O_3 and MnO_2, the actual composition of the residue depending on the manner of ignition. This mixture of oxides may be converted quantitatively into—

(1) MnO (green), by heating to a high temperature in a current of hydrogen ;
(2) Mn_3O_4 (brown), by heating to a high temperature in a current of carbon dioxide ;
(3) Mn_2O_3 (black), by heating to low redness in a current of oxygen ;
(4) MnS (green), by heating with sulphur in hydrogen ;
(5) $MnSO_4$ (white), by adding sulphuric acid and heating to low redness.

Procedure.—If the manganese is present as permanganate it must first be reduced to a manganous salt by means of sulphur dioxide and the excess of sulphur dioxide expelled by boiling.

Neutralise the solution with ammonia, add 10 grams of ammonium chloride and a slight excess of ammonium carbonate. Allow the beaker to remain on a gently heated steam-bath until the precipitate has settled completely. Filter,

and wash the precipitate with hot water. Incinerate the filter together with the precipitate in a Rose crucible, and ignite the precipitate in the open crucible for ten minutes with a Méker or Teclu burner. Then pass a slow current of carbon dioxide into the crucible, and heat again to a high temperature for ten minutes. Cool in an atmosphere of carbon dioxide, and weigh as Mn_3O_4. Repeat until constant weight is attained.

In order to check the result, heat the oxide with a Méker burner in a *rapid* current of hydrogen for five minutes, and weigh as MnO. Repeat until the weight is constant.

Determination of Manganese as Oxide after Precipitation as Dioxide

OUTLINE OF METHOD.—The manganese is precipitated as hydrated manganese dioxide by boiling an acidified solution with ammonium persulphate. The dioxide is converted by ignition into a lower oxide, which is weighed.

Hydrated Manganese Dioxide is a brownish-black precipitate which is insoluble in water, alkalis, dilute sulphuric or nitric acid. It is somewhat soluble in concentrated nitric acid, readily soluble in hydrochloric acid with evolution of chlorine, and in concentrated sulphuric acid with evolution of oxygen. It is insoluble in solutions of ammonium salts. If precipitated in alkaline solution, it occludes alkali which cannot be removed by washing. The dioxide itself is unsuitable for weighing, and is always converted into one of the lower oxides by ignition, as described above.

Procedure.—Dilute the solution, which should be slightly acid with sulphuric acid, but must contain no other acid, to 200 ml. To the cold solution, add 2 grams of ammonium persulphate dissolved in about 50 ml. of water, and heat quickly until boiling. Add ammonia until the solution is faintly alkaline. Boil for two minutes, filter at once without cooling, and wash the precipitate thoroughly with hot water. The filtrate should be colourless ; set it aside on the steam-bath for an hour. No further precipitate should form, but if there is any, filter, and add it to the main precipitate.

Incinerate the filter together with the precipitate in a Rose crucible, and convert into a lower oxide suitable for weighing, as described above.

The above method affords a complete separation from chromium. If other metals, such as iron, zinc, nickel, and cobalt are present, a second precipitation is necessary, and even then the separation may not be complete. Dissolve the precipitate, after thorough washing, in hot concentrated hydrochloric acid containing a little sulphurous acid. Add 1 ml. of concentrated sulphuric acid, evaporate until the hydrochloric acid is expelled, cool, and dilute with water. Reprecipitate as before.

Notes.—(1) The conditions for the precipitation must be closely adhered to, otherwise precipitation is incomplete.

(2) The purity of the ammonium persulphate should be tested. There should be no precipitation of alumina when a solution is boiled with ammonia. No weighable residue should be left after ignition of 2 grams in a platinum crucible.

MERCURY

Forms in which Mercury is precipitated

Mercuric Sulphide.—The mercury must all be present as a mercuric salt. This method is recommended when applicable, *i.e.* in absence of those metals that are precipitated in a similar manner.

Mercury Zinc Thiocyanate.—This is a convenient method for determining mercuric mercury, but in addition to metals which give insoluble thiocyanates, bismuth, cobalt and nickel must be absent as they would be partially precipitated.

Metallic Mercury.—This method is useful for separating mercury from all other metals. It is applicable to mercury in any form of combination.

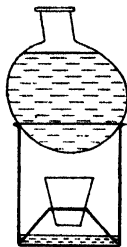
Determination of Mercury as Sulphide

OUTLINE OF METHOD.—The mercury is precipitated with hydrogen sulphide in acid solution, and, after removal of any free sulphur by extraction with carbon disulphide, is weighed as HgS.

Mercuric Sulphide is inappreciably soluble in boiling dilute acids. It is slowly converted into mercury thionitrate and finally into soluble mercuric nitrate by boiling concentrated nitric acid. It may be dried completely at 100°; at higher temperatures it volatilises unchanged.

Procedure.—The mercury, if not already in the mercuric state, must be oxidised by boiling with concentrated nitric acid. The presence of nitric acid in the solution is objectionable, because it gives sulphur with hydrogen sulphide, but it is not permissible to remove it by evaporation with hydrochloric acid since mercuric chloride would be volatilised in the process.

FIG. 65.

Saturate the cold solution with hydrogen sulphide, filter through a Gooch or sintered glass crucible, wash with cold water and then two or three times with alcohol. The sulphur in the precipitate is removed by extraction with carbon disulphide. Carbon disulphide usually contains some dissolved sulphur, and the following method of extraction is therefore recommended :—Place the crucible on a glass triangle within a beaker which contains some carbon disulphide. Cover the beaker with a flask containing cold water (see Fig. 65), and heat the beaker on the steam-bath. (If a water-bath heated with a flame is used, care must be taken that vapour of carbon disulphide does not escape in any quantity.) Within an hour all the sulphur will be extracted. Wash twice with alcohol to remove carbon disulphide, and dry at 100° to 110°. Weigh the HgS.

Determination of Mercury as Mercury Zinc Thiocyanate

OUTLINE OF METHOD.—The solution of the mercuric salt is treated with excess of a solution containing zinc sulphate and ammonium thiocyanate. The precipitated mercury zinc thiocyanate is collected on a sintered glass crucible, washed, dried, and weighed.

Mercury zinc thiocyanate is a white solid, very sparingly soluble in water. It is soluble in ammonium salts and in strongly acid solution. If the mineral acid concentration is greater than decinormal, it must be nearly neutralised with sodium hydroxide. If the mercury compound is not already in the mercuric state, it must be boiled with a *little* concentrated nitric acid, and the solution *almost neutralised, after* dilution.

Procedure.—Weigh accurately about 0·25 gram of mercuric chloride into a 250 ml. beaker, add 75 ml. of water, and 1 ml.

of dilute hydrochloric acid. While stirring vigorously add 25 ml. of the reagent, prepared by dissolving 3·9 grams of ammonium thiocyanate and 2·9 grams zinc sulphate in water and diluting to 100 ml. A precipitate gradually separates, and it should be allowed to stand several hours or overnight before filtering. Filter on a No. 3 sintered glass crucible, wash four times by decantation, using about 20 ml. portions of a washing liquid made by diluting 5 ml. of the precipitating reagent with 450 ml. of water. Transfer the precipitate to the crucible using this liquid in a washing bottle, and finally wash the precipitate in the crucible three times with small amounts of water. Dry the precipitate in an air oven at 105° to 110°; slight decomposition occurs at 120°.

Determination of Mercury as Metal

(1) OUTLINE OF METHOD.—The dry substance is heated with a mixture of quicklime, iron filings, and lead chromate. The mercury that is driven off is collected and weighed.

Procedure.—A convenient apparatus is that devised by Penfield for the determination of water in minerals. Close a

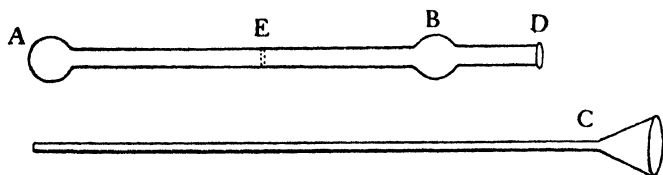



FIG. 66.

piece of glass tubing (about 20 cm. in length and 5 mm. in diameter) at one end, and blow bulbs at A and B (Fig. 66).

Clean, dry, and weigh the tube. By means of the long funnel C, introduce 0·5 to 1·0 gram of the powdered material into the bulb A. Weigh the tube and contents.

Add some iron filings by means of the funnel C, from which any adhering trace of the substance has meanwhile been removed. Mix the substance and filings thoroughly by rotating the tube. Then add a mixture of one part quicklime, one part powdered (fused) lead chromate, and two parts iron filings, until about 8 cm. of the tube has been filled. Insert a small plug of asbestos, E, so that, after tapping the tube, only a very

shallow air-channel remains over the mixture. Draw out the open end D into a fine capillary, as shown at F, Fig. 67.

Place the prepared tube in an iron tube that can be heated by a flat-flame burner. (A piece of iron gas-pipe about 15 cm. by 1·5 cm., closed at the ends with plugs of asbestos, may be used.) Wrap the bulb A in some asbestos paper to prevent it coming into direct contact with the iron tube; if this precaution is omitted, the bulb becomes hot before the narrow portion of the tube, and the mercuric salt is partly volatilised without decomposition. Place an asbestos shield at G, and cover the bulb B with wet filter paper.

Heat the iron tube, at first with a small flame and at the end nearer G only. Gradually increase the flame and move it until the whole iron tube is heated to a low red heat. The

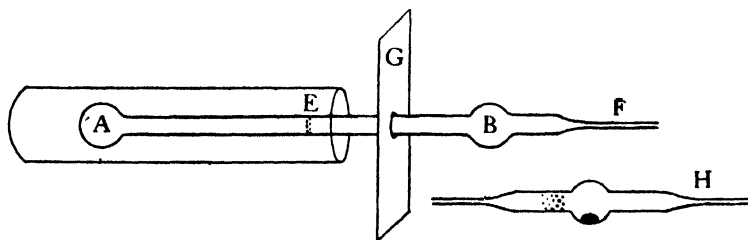



Fig. 67.

apparatus must be almost horizontal, but with the end F slightly lower than the closed end, so that, on gently tapping the tube, any mercury that has condensed forms a globule and runs into the bulb B.

When all the mercury has distilled (usually within one hour), draw out the glass tube until the plug E is exposed. At the same time move the burner forward, so that the flame plays directly on the glass tube. As soon as the glass tube becomes red hot, draw it out and cut it off about midway between the plug E and the bulb B. The mercury is thus obtained in a tube, as shown at H in Fig. 67.

To remove water, draw a current of dry air through the tube until the weight is constant. Shake out the main portion of the mercury, and remove the remainder by blowing air through the gently heated tube. (**Caution.**—*Mercury vapour is poisonous.*) Weigh the empty tube after cooling.

(2) OUTLINE OF METHOD.—The salt of mercury is reduced to metal by boiling with glycerol in the presence of alkali. The mercury is filtered off through a Gooch or sintered glass crucible, and either weighed as such, or dissolved in nitric acid and determined volumetrically.

Procedure.—Dissolve the mercury salt, containing about 0·25 gram of mercury, in a very little hot water in a small beaker. Add 15 ml. of a 30 per cent. solution of sodium hydroxide, and 10 ml. of glycerol. Boil for five minutes, cool, and dilute with an equal volume of water. Filter through a fine Gooch or sintered glass crucible, wash well with water, and then with acetone. Dry at 60°.

Instead of washing with acetone and weighing, the mercury may be dissolved in hot concentrated nitric acid diluted with an equal volume of water, and determined volumetrically as described on p. 180.

MOLYBDENUM

Molybdenum may be determined volumetrically, but is more commonly determined by a gravimetric method.

Forms in which Molybdenum is precipitated

Molybdenum Sulphide.—This method involves the previous separation of tungsten if present, but vanadium does not interfere.

Mercurous Molybdate.—This is obtained by the addition of mercurous nitrate to a molybdate, a process similar to that used with a tungstate (p. 355). It requires, however, more care in conversion to the trioxide than is the case with mercurous tungstate, since molybdenum trioxide is more volatile than tungsten trioxide.

Lead Molybdate.—This compound may be precipitated in the presence of most of the metals, but vanadium and tungsten must be removed previously.

Determination of Molybdenum as Lead Molybdate

OUTLINE OF METHOD.—Lead molybdate is precipitated by the addition of lead acetate to a solution of ammonium molybdate containing ammonium acetate and acetic acid. The precipitate is filtered, washed, ignited, and weighed.

Lead Molybdate, $PbMoO_4$, is a white solid, insoluble in acetic acid, and unaltered by ignition even in contact with filter paper.

Procedure.—Weigh out accurately about 0·1 gram of ammonium molybdate. Dissolve it in about 200 ml. of water, add 15 ml. of 2N HCl, and 10 grams of ammonium acetate. Heat to boiling, and run in 10 per cent. lead acetate solution from a burette whilst stirring until no further precipitation takes place. About 5 ml. should be sufficient. Heat on the water-bath for a few minutes, and filter through ashless paper whilst hot. Wash with a hot 1 per cent. solution of ammonium acetate until the washings give no turbidity with potassium chromate. Dry the filter and ignite it in a porcelain crucible at as low a temperature as possible until all carbon has been burnt away. Cool, and weigh.

NICKEL

Nickel is determined after removal of metals that are precipitated by hydrogen sulphide in acid solution. Although a pure nickel solution yields no precipitate with hydrogen sulphide in acid solution, some nickel is co-precipitated with the sulphides of the copper and arsenic group unless the solution is strongly acid.

A colorimetric method for the determination of traces of nickel is described on p. 259.

Forms in which Nickel is precipitated

Nickel Sulphide.—Ammonium monosulphide precipitates nickel, together with the other metals of the iron and zinc group, and this method serves to separate nickel, iron, zinc, etc., from the alkalis and alkaline earths. Nickel sulphide is not precipitated from acid solutions, but the precipitated sulphide dissolves very slowly in cold dilute acids.

Nickel Peroxide.—This is a form in which nickel may be precipitated if no other metals are present.

Nickel Salt of Dimethylglyoxime.—Nickel is precipitated in this form from alkaline or acetic acid solutions by means of an alcoholic solution of dimethylglyoxime. This method separates nickel from cobalt, zinc, manganese, and (with appropriate modification) from iron, aluminium, chromium, and copper.

Metallic Nickel (Electrolytic).—This is a useful and accurate method for the determination of nickel. The method

can be adapted to provide a separation of nickel from copper and other metals (see p. 248).

Determination of Nickel as Oxide after Precipitation as Peroxide

OUTLINE OF METHOD.—The nickel is precipitated as nickel peroxide by means of bromine and sodium hydroxide. The precipitate is washed, dried, and ignited. It is then ignited in an atmosphere of hydrogen and the metallic nickel weighed.

Nickel Peroxide, Ni_2O_3, when freshly precipitated, is a brownish-black substance which becomes darker on keeping. It is insoluble in hot or cold water and in alkaline solutions. The peroxide, unlike nickelous hydroxide, does not occlude alkali salts. On ignition, it is converted almost entirely into nickel oxide, NiO, but the composition of the residue varies considerably with the manner of ignition. Nickel oxide is completely reduced to metal by ignition in hydrogen. The metallic nickel may be contaminated with silica dissolved from the glass or porcelain vessel by the sodium hydroxide.

Procedure.—Dilute the nickel solution, which must not contain ammonium salts, in a porcelain beaker or basin to about 100 ml., and add about 1 ml. of bromine. Warm the solution, and precipitate the nickel with pure sodium hydroxide solution, avoiding excess. Heat until boiling. Any signs of greenish, nickelous hydroxide indicate that insufficient bromine has been added.

Filter, wash the precipitate with hot water (as far as possible by decantation), and dry. Incinerate the filter paper apart from the precipitate in a Rose crucible, add the precipitate, and ignite strongly for a few minutes. Allow the crucible to cool; pass a current of pure, dry hydrogen (see p. 214) and heat the crucible to dull redness for about twenty minutes. Continue the current of hydrogen until the crucible is cold, in order to prevent reoxidation. Repeat the ignition in hydrogen until the weight has become constant. The metallic nickel obtained in this way contains traces of silica. If the precipitation has been performed in a porcelain vessel without using a large excess of alkali, the amount of silica will be very small; but in all cases the silica should be determined and a correction applied. Dissolve the nickel in nitric acid, and evaporate to

dryness. Moisten the residue with a few drops of concentrated acid, dilute with water, filter through a small filter paper, and wash until the residue is colourless. Incinerate the paper with the residue of silica, ignite, and weigh. Subtract the weight of silica from that of the impure nickel.

Determination of Nickel by the Dimethylglyoxime Method

OUTLINE OF METHOD.—The nickel is precipitated by adding dimethylglyoxime dissolved in alcohol to a hot, slightly acid solution, and then adding ammonia or sodium acetate. The precipitate is collected in a Gooch or sintered glass crucible, dried at 120°, and weighed as $(C_4H_7N_2O_2)_2Ni$.

Dimethylglyoxime,

$$CH_3.C(NOH).C(NOH).CH_3 \text{ or } C_4H_8N_2O_2,$$

is a white, crystalline substance, insoluble in water. The reagent is a 1 per cent. solution in absolute alcohol. It precipitates nickel as a voluminous, scarlet, crystalline salt, $(C_4H_7N_2O_2)_2Ni$, easily soluble in mineral acids, but practically insoluble in water, acetic acid, and dilute ammonia. It is soluble in solutions containing a high percentage of alcohol.

Procedure.—Dilute the solution (which should contain not more than 0·05 to 0·06 gram of nickel, and should be slightly acid) to 200 ml. and heat to about 80°. Add an excess of the reagent (20 to 30 ml.), and then add ammonia until the solution is very slightly alkaline (or add 2 to 3 grams of sodium acetate). Keep the solution hot for a few minutes, cool, and allow to stand for not more than an hour, filter through a Gooch or sintered glass crucible, and wash the precipitate with hot water. Dry at 120° for an hour, and weigh. The precipitate contains 20·32 per cent. of nickel.

If cobalt is present, dilute the solution before precipitation so that 200 ml. contains not more than 0·1 gram of cobalt, and add at least 50 ml. of the reagent for 0·05 gram of nickel.

If copper is present, add sufficient ammonia to form the blue, soluble cuprammonium salt before precipitating the nickel. Filter and wash the precipitate. Dissolve it in hot nitric acid (1 : 3), and reprecipitate the nickel in presence of ammonia as before.

If zinc is present, add sufficient ammonium chloride to prevent precipitation of the zinc by ammonia.

If iron, aluminium, or chromium is present, add sufficient tartaric acid (1 to 3 grams) to prevent their precipitation as hydroxides, dilute to 300 ml., and add a large excess of the reagent.

If manganese is present, add sodium acetate (not ammonia) to complete the precipitation of the nickel complex.

NITRATE

Volumetric methods for the determination of nitrate are described on pp. 95 and 109, and a gas-volumetric method on p. 430.

The determination of traces of nitrate in natural waters is described on pp. 458 and 460.

NITRITE

A volumetric method for the determination of nitrite is described on p. 108, and gas-volumetric methods on pp. 430 and 432.

The determination of traces of nitrite in natural waters is described on p. 457.

PHOSPHATE

Forms in which Phosphate is precipitated

Ammonium Phospho-molybdate.—The chief value of this method is that it is applicable in presence of the alkaline earths, aluminium, and iron.

Magnesium Ammonium Phosphate.—This method is not applicable in presence of metallic radicals other than the alkalis.

Determination of Phosphate by the Molybdate Method.

OUTLINE OF METHOD.—The phosphate is precipitated in presence of nitric acid by ammonium molybdate. The precipitate is collected in a Gooch or sintered glass crucible, ignited, and weighed as phospho-molybdic anhydride, $24MoO_3, P_2O_5$.

Ammonium Phospho-molybdate, $(NH_4)_3PO_4, 12MoO_3, xH_2O$,

is a bright yellow crystalline substance, insoluble in dilute nitric and sulphuric acids, but somewhat soluble in hydrochloric acid. It is readily soluble in ammonia, and soluble also to some extent in solutions containing chlorides or ammonium salts (except the nitrate).

It may be weighed as the anhydrous salt after drying at 180°, but it is better to convert it into phospho-molybdic anhydride, $24MoO_3$, P_2O_5, by gentle ignition. The anhydride must not be heated too strongly, otherwise phosphoric anhydride will be volatilised and lost. Ammonium phospho-molybdate may also be determined indirectly by an alkalimetric method (p. 96).

On account of the small proportion of phosphorus in the final precipitate, an amount of substance containing about 10 mgrms. of P_2O_5 is ample for an analysis.

The following solutions are required :—

(1) *Ammonium Molybdate.*—Dissolve 3 grams of the powdered crystals in 100 ml. of water.

(2) *A Washing Solution* containing 50 grams of ammonium nitrate and 40 ml. of concentrated nitric acid per litre of water.

Preparation of a Solution for Analysis.—As a rule, all the phosphorus can be obtained in solution by boiling the substance with concentrated nitric acid. For complex rocks containing silicates, however, fusion with sodium carbonate is necessary, and the silica must be removed by evaporation to dryness in presence of nitric acid.

The phosphorus must be in the form of ortho-phosphate ; meta- or pyro-phosphates must therefore be boiled with dilute nitric acid for a few minutes.

Procedure.—Place a measured volume of the phosphate solution containing about 10 mgrms. of P_2O_5 in a 400 ml. beaker, add 10 grams of ammonium nitrate, and 5 ml. of concentrated nitric acid. Add water to give a final volume of about 100 ml. Measure 50 ml. of the 3 per cent. ammonium molybdate solution into a flask. Heat the two solutions to between 40° and 45°, and add the ammonium molybdate solution slowly to the phosphate mixture. using a dropping-tube (p. 236). Stir continuously for a few minutes, but avoid touching the sides of the beaker with the stirring-rod. After about twenty minutes, filter through a Gooch or sintered glass crucible, and wash with 60 to 80 ml. of the prescribed washing solution.

Place the crucible inside a larger metal crucible in which a perforated porcelain disc is first placed. Heat the outside crucible very carefully to dull redness until the precipitate has a uniform greenish-black colour. Weigh the phospho-molybdic anhydride obtained.

Determination of Phosphate as Magnesium Pyrophosphate, after Precipitation as Magnesium Ammonium Phosphate

OUTLINE OF METHOD.—The phosphate is precipitated by addition of "magnesia mixture" as magnesium ammonium phosphate, which is converted by ignition into magnesium pyrophosphate, $Mg_2P_2O_7$.

Magnesium Ammonium Phosphate, $MgNH_4PO_4$.—The properties of this precipitate and the conditions under which it may be obtained pure, are described on p. 314. The precipitate has the composition corresponding to the normal salt, $MgNH_4PO_4$, only when these conditions are rigidly adhered to.

Magnesium Pyrophosphate, $Mg_2P_2O_7$, has already been described (p. 314).

Procedure.—The following method is based on the procedure recommended by Epperson (*J. Amer. C. S.*, 1928, vol. 50, p. 329), and modified by Hoffmann and Lundell (*Bureau of Standards*, *J. Res.*, 1930, vol. 5, p. 282).

To a neutral or weakly acid solution of an ortho-phosphate, containing not more than 0·1 gram of P_2O_5, add 5 ml. of concentrated hydrochloric acid, and 1 ml. of methyl red indicator. Dilute the solution to 150 ml., and add 10 ml. of a solution prepared by dissolving 5 grams of $MgCl_2.6H_2O$ and 10 grams of NH_4Cl in water, adding 5 ml. of normal hydrochloric acid, and diluting to 100 ml. After adding the magnesia solution, cool well, and neutralise while stirring with ammonia. The procedure from this stage is the same as that described under the determination of magnesium (p. 315), except that when carrying out the reprecipitation from the hydrochloric acid solution, 2 ml. of the above "magnesia mixture" are added instead of 1 ml. of ammonium phosphate solution.

PLATINUM

Platinum when alloyed with gold or silver is usually determined by a dry assay involving cupellation. If present together with other metals of the platinum group, the process

of its determination is complex. In either of these cases special books must be consulted.

Forms in which Platinum is precipitated

Ammonium Chloroplatinate, $(NH_4)_2PtCl_6$. This is a yellow, crystalline, sparingly soluble compound, 100 grams of water dissolving 0·7 gram at 10°. It is almost insoluble in alcohol. It may be weighed as such, or it may be ignited and the resulting metallic platinum weighed. The former procedure is preferable, as platinum may be lost during the combustion of the filter paper owing to the formation of a volatile compound of platinum chloride and carbon monoxide.

Metallic Platinum.—This is obtained by reduction with magnesium and dilute hydrochloric acid, or with formic acid.

Platinum Sulphide, PtS_2.—This is precipitated by hydrogen sulphide from a solution of chloroplatinic acid. It is soluble in yellow ammonium sulphide. It gives metallic platinum upon ignition.

Determination of Platinum as Ammonium Chloroplatinate

OUTLINE OF METHOD.—A solution of chloroplatinic acid is treated with ammonium chloride solution and alcohol, and the ammonium chloroplatinate precipitated is filtered on a Gooch or sintered glass crucible and weighed.

If the determination is to be made on a sample of metal which has only small amounts of impurity, weigh 0·05 to 0·1 gram into a small porcelain dish. Add 10 ml. of concentrated hydrochloric acid and 3 ml. of concentrated nitric acid, cover the dish, and heat on a water-bath. Add more acid if the metal does not dissolve completely. Evaporate as far as possible on the water-bath, cool, and add 3 ml. of concentrated hydrochloric acid. Evaporate again as far as possible, and repeat the treatment in order to ensure complete removal of nitric acid.

If the determination is to be made on a solution of chloroplatinic acid, measure out an amount containing 0·05 to 0·1 gram of platinum into a small porcelain dish, and evaporate as far as possible on a water-bath.

Dissolve the residue in the dish in about 1 ml. of water, add one or two drops of dilute ammonia until the liquid just smells,

and then make the liquid just acid with dilute hydrochloric acid. Add excess (1 to 2 ml.) of ammonium chloride solution, and 15 ml. of industrial alcohol. Cover the dish with a watch-glass, place over it an inverted beaker, and leave it standing overnight in a cool place. Transfer the precipitate to a Gooch or sintered glass crucible with 80 per cent. alcohol, using a rubber-tipped rod to assist the operation. Wash the precipitate with 80 per cent. alcohol until 1 ml. of the filtrate leaves no residue when evaporated. Finally, wash with acetone, and dry in an oven at 60°. Cool and weigh as $(NH_4)_2PtCl_6$.

If the chloroplatinic acid to be determined contains considerable amounts of impurity, it is advisable to reduce the platinum to the metallic state by the addition of magnesium to the acid solution. The completion of the precipitation may be judged by the disappearance of the yellow colour. Filter the solution, wash the metallic platinum, and ignite with the filter in a small dish. After cooling, dissolve in aqua regia and determine the platinum as described above.

POTASSIUM (AND SODIUM)

Potassium and sodium usually occur together. Lithium also is often present, and in this case the lithium must first be separated from the potassium and sodium as described on p. 312. Either sodium or potassium may be determined in the presence of small amounts of the other metal by a direct method. Alternatively both may be weighed together as chlorides, and either metal determined directly, the other being found by difference.

The preliminary extraction of sodium and potassium in an insoluble silicate is described on p. 388.

Forms in which Potassium is precipitated

Potassium Chloroplatinate.—Ammonium salts and all metals other than sodium and potassium must be removed. Sulphate and phosphate must also be removed.

Potassium Perchlorate.—The special advantages of this method are that the use of expensive platinum salts is avoided, and that it is applicable in presence of phosphate and of most metals. The only common acidic radical that must be removed is sulphate. Ammonium salts must be removed.

Dipotassium Sodium Cobaltinitrite.—This method is sometimes useful because it is applicable in presence of sulphate. Ammonium salts must be removed.

Preparation of a Solution for Analysis

(1) *In the Complete Analysis of a Mixture*, all other metals, including lithium, must be removed prior to the determination of sodium and potassium. (See Lithium, pp. 312 and 313.) If other metals are absent, but any sulphate or phosphate is present, add barium hydroxide solution in slight excess and, without filtration, evaporate to about 50 ml. Add a few drops of freshly prepared ammonium carbonate solution in order to precipitate the barium excess, filter through a small filter paper, and wash with hot water. Determine the sodium and potassium in the filtrate.

(2) *If only Potassium is to be determined*, extract a weighed sample of the original material with hot, dilute hydrochloric acid, and filter from any insoluble matter. (With many minerals, particularly silicates, it is not possible to bring the potassium into solution by treatment with hydrochloric acid. The procedure for a case of this kind is described on p. 388.) Evaporate the solution of mixed chlorides to dryness in a porcelain basin, and heat on a sand-bath to barely visible redness for about fifteen minutes, in order to convert iron, aluminium, etc., into insoluble basic salts. The duration of the ignition should be such that, on extracting the residue with water, a colourless solution, free from iron, is obtained.

When sulphate is present, it must be removed (except for the cobaltinitrite method) after the evaporation to dryness and extraction, by adding a slight excess of barium hydroxide solution, and completing the evaporation and ignition as described above.

Extract the soluble alkali salts by repeated treatment with boiling water, breaking up the insoluble residue as much as possible with a glass rod. Filter into a glass evaporating basin, and determine the potassium by the perchlorate method.

Determination of Potassium as Chloroplatinate

OUTLINE OF METHOD.—After removal of sulphate, phosphate, ammonium salts, and all metals other than sodium and potassium, hydrochloroplatinic acid is added, and the solution is evaporated to dryness. The residue is extracted with methyl alcohol, which dissolves the sodium chloroplatinate. The insoluble residue of potassium chloroplatinate is dried and weighed.

Potassium Chloroplatinate, K_2PtCl_6, is a golden-yellow, crystalline salt. It is sparingly soluble in water, and nearly insoluble in methyl alcohol and in ethyl alcohol. At 20°, 100 grams of each of these solvents, in the order named, dissolves 770 mgrms., 2·7 mgrms., and 1 mgrm. The precipitate obtained in quantitative analysis is, after washing and drying, not pure K_2PtCl_6; it is, however, of constant composition, if the working conditions are always the same. By adopting the procedure described below, the precipitate contains 16·02 per cent. of potassium (calculated for K_2PtCl_6, K = 16·08 per cent.).

As ammonium chloroplatinate is also insoluble in alcohol, it is essential to remove all ammonium salts prior to the precipitation, and also to guard against contamination of the solution by ammonia from the laboratory atmosphere during the analysis.

Sodium Chloroplatinate, Na_2PtCl_6, $6H_2O$, is an orange-red salt which is soluble in absolute ethyl alcohol, somewhat more soluble in absolute methyl alcohol, and readily soluble in water. The hydrated salt becomes anhydrous at the temperature of the steam-bath. The anhydrous salt is less soluble in absolute alcohol than the hydrated salt. In order to separate sodium and potassium chloroplatinates, it is best to use absolute *methyl* alcohol.

Procedure.—The solution, after removal of sulphate, phosphate, and all metals other than sodium and potassium is evaporated to dryness. The sodium and potassium are obtained finally in a platinum crucible as pure chlorides, and weighed. Full details of the procedure up to this stage are given on p. 338. The potassium is then determined as chloroplatinate, as follows :—

Dissolve the mixed chlorides in 5 ml. of water and transfer the solution, with the rinsings of the crucible, to a small porcelain basin.

Both the sodium and potassium chlorides must be converted into chloroplatinates, because sodium chloride is insoluble in alcohol. In order to calculate the amount of hydrochloroplatinic acid required to effect this, the assumption is made that the whole of the chloride is *sodium* chloride. Since the reagent contains 10 per cent. of platinum (see p. 476), 1·7 ml. is required for 0·1 gram of sodium chloride, and the volume of reagent required is found by multiplying the weight of the mixed chlorides by 17.

To the solution of the mixed chlorides add 0·3 ml. more than the calculated quantity of hydrochloroplatinic acid, and place the basin on the steam-bath. Add more water, if necessary, to dissolve any precipitated potassium chloroplatinate that may remain after the solution has become warm. Evaporate until the liquid is syrupy and becomes solid on cooling.

Add about 5 ml. of absolute methyl alcohol [1] to the residue and break up the mass thoroughly with a platinum spatula or glass rod. Decant the liquid through a Gooch or sintered glass crucible that has been dried at 180° and weighed. The solid must be kept as far as possible in the basin, only the clear liquid being poured into the filter. Repeat this treatment with successive *small* quantities of methyl alcohol (grinding up the precipitate each time as thoroughly as possible) until the filtrate is colourless. Transfer the precipitate to the crucible. Wash the sides of the crucible five or six times with small quantities of alcohol, drain off the alcohol thoroughly, dry at 160°, and weigh.

The weight of the precipitate multiplied by 0·1602 gives the weight of potassium, and multiplied by 0·3055 gives the weight of potassium chloride.

Determination of Potassium as Perchlorate

OUTLINE OF METHOD.—The solution of mixed chlorides is evaporated almost to dryness with perchloric acid. All salts other than potassium perchlorate are then extracted with alcohol, and the insoluble residue is weighed.

Potassium Perchlorate, $KClO_4$, is a sparingly soluble, crystalline salt. At 25°, 100 grams of water dissolves 2·08 grams

[1] Although less satisfactory, 95 per cent. ethyl alcohol (by volume) may be used.

of the salt, 100 grams of 99 per cent. alcohol dissolves 19 mgrms., and 100 grams of 98 per cent. alcohol containing 0·2 per cent. of perchloric acid dissolves 10 mgrms. The solubility decreases rapidly with falling temperature, and 100 grams of the last-named solvent at 10° dissolves only about 3 mgrms. The salt may be dried without decomposition above 100° and below 200°.

Sodium Perchlorate is a white salt which is readily soluble in water and alcohol.

Procedure.—To the solution of the mixed potassium and sodium chlorides, add 10 ml. of 20 per cent. perchloric acid. (If the mixed chlorides weigh less than 0·2 gram, 5 ml. may be sufficient.) Evaporate the solution, in a quartz or "resistance" glass basin, *almost* to dryness. The evaporation is performed on a sand-bath or, preferably, on a shallow sand-bath tray covered with a set of rings. Add another 5 ml. of perchloric acid and again evaporate practically to dryness. If copious evolution of perchloric acid (white fumes) is not observed towards the end of the evaporation more acid must be added and the evaporation repeated. (The amount of perchloric acid used must be more than sufficient to convert all the salts into perchlorates.)

Prepare two washing solutions as follows:—(*A*) Add 0·3 ml. of 60 per cent. perchloric acid to 100 ml. of "absolute" alcohol; for this solution make a special "wash-bottle" from an ordinary test-tube—the outlet tube and *fine* jet being made from a single piece of glass tubing. (*B*) Saturate 100 ml. of rectified spirit with potassium perchlorate; the alcohol and perchlorate crystals must be vigorously shaken in a stoppered bottle for several minutes immediately before decanting or filtering a portion for use.

Prepare a Gooch crucible—using somewhat more asbestos than usual—or a sintered glass crucible and fit the adapter into a filter-tube (a test-tube with side-tube) instead of the usual filter-flask.

To the almost dry, *cold* residue add 10 ml. of washing solution (*A*), stir well with a flat-ended glass rod and set aside for about five minutes with occasional stirring. Allow the potassium perchlorate to settle, and decant through the crucible. *Do not heat or explosion may occur.* (Reject the filtrate.)

Dissolve the perchlorate in the minimum amount of hot

water,[1] and evaporate to dryness on the steam-bath. *Cool thoroughly*, add 10 ml. of washing solution (*A*), stir, and decant through the filter. Transfer the perchlorate to the crucible with the minimum amount (10 to 20 ml.) of the washing solution (*A*). Remove with a rubber-tipped rod (p. 35) the perchlorate adhering to the side of the basin ; this requires special care, because it is not easily seen while the basin is wet. Finally, wash the filter five or six times by running into it from a small pipette successive portions (3 ml.) of washing solution (*B*). The total volume of the filtrate (excluding the initial 10 ml. rejected) should not exceed 40 to 50 ml.

Dry for one hour at 130° to 150°, cool, and weigh. Wash again with 2 to 3 ml. of washing solution (*B*), dry, and weigh.

Determination of Potassium as Dipotassium Monosodium Cobaltinitrite

OUTLINE OF METHOD.—The solution containing potassium and sodium chlorides (nitrates or sulphates) is evaporated to dryness with an excess of sodium cobaltinitrite. The residue is extracted with acetic acid, washed with water, dried, and weighed.

Dipotassium Monosodium Cobaltinitrite,

$$K_2NaCo(NO_2)_6 , H_2O,$$

is a lemon-yellow, crystalline salt, very sparingly soluble in water and in dilute acetic acid. The monohydrate is stable at 100°. The precipitate only has the above composition when the atomic ratio of sodium to potassium is greater than 22 : 1 during precipitation.

The sodium cobaltinitrite reagent is prepared as follows :—Dissolve 28 grams of cobalt acetate in a mixture of 75 ml. of water and 25 ml. of glacial acetic acid, and add a solution of 55 grams of sodium nitrite in 100 ml. of water. Warm the mixture gently in a round-bottomed flask and evacuate the flask to remove oxides of nitrogen. Set the solution aside for twenty-four hours. (A slight yellow precipitate usually separates because sodium nitrite is rarely free from potassium salts.) Filter, and dilute the solution to 250 ml. The solution should be kept in the dark.

Procedure.—To the solution of the mixed potassium and sodium salts (containing, preferably, not more than 0·1 gram

[1] This is omitted if sodium is absent.

of the potassium salt), add an excess of the reagent (not less than 20 ml.) and evaporate to dryness on the steam-bath. After cooling, stir the residue with 5 per cent. (approximately normal) acetic acid, allow the precipitate to settle, and decant through a Gooch or sintered glass crucible. Wash the precipitate by decantation with acetic acid, transfer it to the crucible, and wash with cold water until free from acid. Dry at 100°, and weigh as $K_2NaCo(NO_2)_6 , H_2O$.

Determination of Potassium and Sodium

OUTLINE OF METHOD.—All metals other than sodium and potassium, and all acid-radicals other than chloride, are removed (see p. 311). The solution is evaporated to dryness, and the residue of mixed chlorides weighed. The potassium is then determined by either the chloroplatinate or the perchlorate method and the sodium found by difference. Alternatively, if the content of potassium is known to be low, the sodium may be determined by means of zinc uranyl acetate (p. 346).

Sodium Chloride is readily soluble in water but is almost insoluble in alcohol. It may be dried completely at 100°, but unless the drying process is very prolonged, it mechanically retains a trace of water which is expelled, with decrepitation, at higher temperatures. Heated to dull redness it melts, and at a bright red heat volatilises rapidly; at all temperatures above the melting-point, there is appreciable loss by volatilisation.

Potassium Chloride very closely resembles sodium chloride in properties, but is slightly more volatile.

Procedure.—Evaporate the solution (from which sulphate phosphate and all other metals, including lithium, have been removed) in a porcelain basin until the bulk is reduced to about 50 ml. Transfer it to a 100 ml. platinum basin and rinse the porcelain basin with hot water. Evaporate to complete dryness on the steam-bath. (The subsequent manipulation is facilitated if the residue is dried at this stage as completely as possible, and it is advisable to heat the covered basin in an air-oven at 120° to 150° for an hour or more.)

Place the basin on a sand-bath and heat—very gently at first—until all moisture is driven off. During this operation, the basin must be kept covered with a clock-glass and the heating interrupted whenever decrepitation begins. When decrepitation has wholly ceased, raise the temperature, but do

not remove the clock-glass. Continue the heating until the clock-glass and the sides of the basin are thickly coated with ammonium chloride.

Remove the clock-glass. Invert it and heat it gently over a small flame until all the ammonium chloride has volatilised, and set it aside to be washed later.

Place the basin on a pipe-clay triangle, and heat the sides of the basin until the ammonium chloride has volatilised. The burner must be held in the hand and the flame kept in constant motion to prevent over-heating and consequent volatilisation of any alkali chloride. Next heat the bottom of the basin in the same manner until no more ammonium chloride is given off. During this process the residue almost invariably blackens owing to the charring of traces of organic impurities from the reagents.

Cool, add about 5 ml. of hot water, and filter through a very small (5½-cm.) filter paper into a tared platinum crucible. *Extreme care is necessary at this stage, since the loss of a single drop of the solution renders the determination valueless.* Wash the basin and filter paper with hot water, using about 2 ml. for each washing. Wash into the crucible also any trace of salt adhering to the clock-glass.

Add one drop of hydrochloric acid and evaporate to complete dryness on the steam-bath. When the residue is apparently dry, remove from the steam-bath and heat the covered crucible with a small flame, observing the same precautions as before against over-heating. Cool, and weigh. Repeat the heating until the weight is constant. (The salt is sometimes dark in colour on account of traces of carbon. The carbon will disappear on prolonged heating, but its weight is negligible.) The weight gives the amount of potassium and sodium chlorides.

Determine the amount of potassium in the mixed chlorides by following the instructions given on pp. 334, 335, or 337, according to the method employed.

Calculate the weight of potassium chloride corresponding to the weight of the chloroplatinate, perchlorate or cobaltinitrite obtained. Subtract the weight of potassium chloride from that of the mixed chlorides in order to find the weight of sodium chloride.

An alternative method consists in dissolving the weighed

mixed chlorides in water, and determining the total chlorine gravimetrically (p. 230). The weight of potassium chloride (x grams), and that of the sodium chloride (y grams), can then be calculated from the equations :—

$$x + y = \text{weight of mixed chlorides,}$$

$$\frac{35 \cdot 46}{74 \cdot 56} x + \frac{35 \cdot 46}{58 \cdot 46} y = \text{weight of total chlorine.}$$

The method is not very accurate, as any error in the determination of the total chlorine is multiplied by a large factor in calculating the values of x and y.

SILICA AND SILICATES

Properties of Silica.—From the analytical point of view, one may distinguish between three varieties of silica : (1) the jelly obtained by the incomplete dehydration of precipitated "silicic acid" ; (2) silica obtained by the ignition of precipitated "silicic acid" ; (3) native silica.

Gelatinous "silica" is readily soluble in alkali hydroxides and carbonates, and appreciably soluble in water and in acids. After ignition, it is practically insoluble in water and in acids (except hydrofluoric acid), but dissolves slowly in alkalis. Native crystalline silica (*e.g.* quartz) is insoluble in acids (except hydrofluoric acid), and is only slowly attacked by alkalis.

The powder obtained by drying gelatinous silica at 100° contains about 13 per cent. of water. Even at 200°, it still retains about 5 per cent. ; only on ignition is the last trace of water expelled. The silica obtained by drying the jelly at 100° dissolves to an appreciable extent in acid, and is not rendered completely insoluble (as is often stated) by repeated evaporation to dryness with hydrochloric acid.

Precipitated silica is hygroscopic unless it has been ignited for at least twenty minutes with a blowpipe or a Méker burner.

Determination of Silica in an Insoluble Silicate

OUTLINE OF METHOD.—The silicate is decomposed by fusion with sodium carbonate or fusion mixture. The fused mass, after cooling, is disintegrated by warming with dilute hydrochloric acid, and the solution is evaporated to dryness on the steam-bath. The residue is dehydrated by baking in an air-oven. Hydrochloric acid and water are added, and the silica, most of which remains insoluble, is separated by filtration. The solution, which still contains a little silica, is evaporated to dryness again, and the residue is treated as before. The silica is then dehydrated by ignition and is weighed as SiO_2.

Procedure.—In a small weighing-bottle place from 0·9 to 1·1 gram of the finely powdered silicate, and weigh accurately. Transfer the powder to a platinum crucible containing about 3 grams of pure, dry sodium carbonate, or fusion mixture. (Reweigh the weighing-bottle to find the weight of silicate taken.) Add to the crucible another 3 grams of sodium carbonate or fusion mixture. Place the crucible on a sheet of glazed paper and mix the contents very thoroughly by stirring gently with a small spatula (preferably of platinum), care being taken that no unmixed silicate remains at the bottom of the crucible.

Cover the crucible, place it on a triangle about 4 inches above a small Bunsen flame, and heat gently for about five minutes. Then lower the crucible and increase the flame gradually so as to melt the contents without any spluttering. Cautiously lift the lid of the crucible at intervals and examine the contents to make sure that there is no excessive frothing. No spatter should be seen on the lid if the fusion has been properly conducted. After heating until a state of quiet fusion is attained, heat the crucible with a Méker burner for about fifteen minutes. When the fusion is complete, the molten mixture may not be perfectly clear, but practically no further escape of gas bubbles should be seen. The whole operation takes from thirty to forty minutes.

Now lift the crucible with platinum-tipped tongs (p. 211) and impart a rotary motion to the vessel as cooling proceeds. In this way, the mixture is made to solidify in a thin sheet on the side and bottom of the crucible, and its subsequent removal from the crucible is thereby facilitated. As a rule the cold cake has bluish-green colour owing to the presence of sodium manganate.

After the crucible has become *quite cold*, half-fill it with water and warm *cautiously* with a very small flame for several minutes; this will often suffice to loosen the cake. Transfer the liquid and the cake to a 15-cm. porcelain basin containing 150 ml. of hot water, and carefully rinse the crucible into the basin to remove as far as possible any adhering portions of the cake. Set the crucible and lid aside for final cleaning at a later stage. If the cake cannot be readily loosened in this way, place the crucible on its side in the porcelain basin together with 150 ml. of hot water, and warm on the steam-bath until the mass is completely detached from the crucible. Remove the crucible, rinse it carefully, and set aside with the lid for final cleaning. Break up the cake as far as possible with a blunt glass rod and then add, very gradually, excess of hydrochloric acid (20 ml. of concentrated acid mixed with 10 ml. of water), the basin being covered with a clock-glass to prevent loss during the decomposition of the carbonate.

When the disintegration is complete and effervescence has ceased, remove the clock-glass, rinsing it into the basin. Clean the crucible and the underside of the lid with a few drops of warm hydrochloric acid and add the rinsings of both to the basin. Evaporate to dryness on the steam-bath. Towards the end of the evaporation, stir frequently in order to break the crust that forms on the surface of the liquid. When the mass is quite dry, heat the basin in an air-oven between 105° and 110° for one hour in order to dehydrate the silica. This is then almost wholly insoluble in acid and the second evaporation of the solution—indicated below—may be omitted except in analyses of the highest accuracy.

Moisten the dry powder with 10 ml. of concentrated hydrochloric acid, stir, and set aside for ten minutes in order that any basic salts (of iron, etc.) may be converted into normal chlorides. Then add about 30 ml. of water and heat on the steam-bath and stir frequently until only the silica remains undissolved. The silica is often in a coarse condition and may be ground finer with a blunt glass rod.

Filter through a 9-cm. paper. Wash the silica several times by decantation with hot dilute acid. (The acid is not put into the wash-bottle but a little is added to the basin with each portion of hot water.) Transfer the silica to the filter. Remove any silica adhering to the basin and stirring-rod with

a small piece of filter paper and add this to the main precipitate. Then wash the precipitate and paper with hot water until a few drops of the washings give no turbidity with silver nitrate.

Some of the silica always dissolves in the hydrochloric acid —probably only a fraction of 1 per cent. of the total silica if the above procedure is followed—and most of this may be recovered by evaporating the filtrate again to complete dryness. The residue is treated with acid, water is added, and the solution filtered through another (smaller) paper. The basin and the filter are washed with hot dilute acid and then with hot water as before.

The filter papers containing the silica are incinerated, without previous drying, in a weighed platinum crucible, heating gently until all the carbon has been burnt away. Then ignite the silica in the covered crucible with the full flame of a Méker burner for at least twenty minutes. Cool, and weigh the SiO_2. Repeat the ignition until constant weight is attained.

The silica obtained in this way is never entirely free from impurities, and it is advisable to determine the amount of impurity by driving off the silica with hydrofluoric acid and weighing the non-volatile residue. To accomplish this, moisten the silica with water, add one or two drops of concentrated sulphuric acid, and 4 to 5 ml. of hydrofluoric acid.[1] (**Caution**: see footnote.) Evaporate to dryness, first on the steam-bath and then with a Bunsen flame (see p. 28 and Figs. 13 and 14). Ignite for two or three minutes with a Méker burner, cool, and weigh.

Pure silica should leave no residue, and the weight of the impurity must therefore be subtracted from the weight of the crude silica. The residue usually contains oxides of aluminium, iron, titanium, and phosphorus, and it may weigh from 2 to 10 mgrms. If a complete analysis of the silicate is being made, the subsequent precipitate of alumina, etc., should be ignited in the crucible containing the impurity found in the silica.

[1] Owing to its action upon glass, hydrofluoric acid is kept in gutta-percha or heavily waxed glass bottles. In the latter case the liquid is obtained by making two holes with a hot iron rod in the wax plug, which must be sealed again afterwards. The liquid, usually about 30 per cent. hydrofluoric acid, should be handled with the ordinary care taken with corrosive acids, and its evaporation must be carried out in a good draught, as its vapour is poisonous.

Notes.—(1) The evaporations for the removal of silica must be continued until the residue forms a *dry powder*. This powder is often very light, and, like ignited silica, is very easily blown away if care is not taken to protect it from draughts.

(2) In accurate work, the weight of the crude silica should always be corrected for impurity. If, however, it is not intended to determine the silica which, in spite of all the precautions described above, escapes precipitation and is found along with the ferric oxide and alumina (see p. 387), the correction should not be applied; instead, the assumption is made that the weight of the impurity is equal to that of the silica which has passed into the filtrate.

(3) The hydrofluoric acid must be free from non-volatile impurities. The acid supplied in waxed bottles is usually pure, but it is advisable to test a sample. A correction must be applied if there is any non-volatile residue after evaporation.

"Silica" as an Insoluble Residue

In many minerals, slags, and technical products, the residue left after treatment with acid is mainly silica. It is often permissible, *e.g.* in analyses made for technical purposes, to report the insoluble residue, without further examination, as "silica" or "silica and insoluble silicates." Typical examples of the determination of "silica," where "silica" means only the portion insoluble in acid, are described under Dolomite (p. 380) and Pyrites (p. 396). In these determinations some of the silica usually dissolves; but, on the other hand, the residue is not entirely silica, and for many purposes the uncorrected results are sufficiently accurate.

When an accurate determination of the silica is required, the following modification is necessary:—The "silica" must be evaporated with hydrofluoric and sulphuric acids and the weight of the non-volatile residue ascertained (p. 343). This residue must then be fused with sodium carbonate, or fusion mixture, and added to the main solution. This must be evaporated to complete dryness, and the small amount of silica present separated in the manner already described (p. 342).

SILVER

The volumetric method for the determination of silver, described on p. 179, is convenient and accurate.

Gravimetrically, silver is usually determined as chloride, but the gravimetric determination as silver bromide is recommended.

Traces of silver in lead can be determined by a method depending on the displacement of the former from solution by means of metallic copper (Evans, *Analyst*, 1926, vol. 51, p. 79).

Forms in which Silver is precipitated

Silver Chloride.—Silver may be determined by this method in presence of all other metals. The silver is precipitated with dilute hydrochloric acid, carefully avoiding unnecessary excess. If a mercurous salt is present, it must be oxidised with concentrated nitric acid prior to the precipitation of the silver. If lead is present, the solution must be diluted so that it contains not more than 0·2 gram of the substance in 150 ml., and the hydrochloric acid must be added very slowly. Otherwise the procedure is identical with that adopted in determining chloride as silver chloride (p. 230).

Silver Bromide.—This method is preferable to the chloride method on account of the lower solubility of silver bromide. The solution is acidified with nitric acid and potassium bromide added until precipitation is complete. The procedure is otherwise identical with the previous method. For the properties of silver bromide, see p. 287.

SODIUM

Sodium may be determined directly by precipitation as the triple salt, sodium zinc uranyl acetate. It is often determined together with potassium (see p. 338), but in cases in which sodium alone is present in combination with volatile acids, it may be determined conveniently as the sulphate, Na_2SO_4.

Determination of Sodium as Sodium Zinc Uranyl Acetate

OUTLINE OF METHOD.—A small volume of the solution containing the sodium salt is stirred with ten times its volume of a zinc uranyl acetate reagent. The triple acetate precipitated is filtered on a Gooch or sintered glass crucible, and after washing with alcohol and ether is dried and weighed as $NaZn(UO_2)_3(C_2H_3O_2)_9, 6H_2O$.

Sodium Zinc Uranyl Acetate, $NaZn(UO_2)_3(C_2H_3O_2)_9$, $6H_2O$, is a yellow crystalline solid. It separates even from a N/500 solution of sodium chloride when this is treated with considerable excess of a reagent consisting of a concentrated solution of zinc and uranyl acetates saturated with the triple acetate. Though fairly soluble in water, the triple acetate only dissolves to the extent of 0·5 gram per litre at 22° in 95 per cent. alcohol. It is slightly more soluble in absolute alcohol. Its solubility in the reagent increases considerably as the temperature rises, so that the temperature of the mixture when filtered during a determination should be approximately the same as that at which the reagent is filtered to remove the triple acetate after saturation.

Since the molecular weight of the triple acetate is very large, the amount of sodium suitable for a determination should not exceed about 15 mgrm., and the volume of the solution containing the sodium salt must also be small (about 2 ml.) in order to precipitate the sodium as completely as possible. The amount of potassium present should not be greater than 15 mgrm. per ml. The ammonium ion does not interfere in reasonable amount, but lithium forms a triple salt less soluble than that of potassium. Barium, calcium, and magnesium do not interfere, but phosphate and arsenate, if present, must first be removed by standing in contact with zinc carbonate for at least six hours.

In preparing the reagent a pure sample of uranyl acetate must be used, as many commercial samples contain considerable amounts of sodium, resulting in a heavy precipitate of the triple acetate with consequent weakening of the reagent. To 175 ml. of water add 5·5 ml. of glacial acetic acid, and heat the mixture to about 80°. Add 20 grams of uranyl acetate (dihydrate) and 60 grams of zinc acetate (trihydrate). After stirring until the salts have dissolved, cool to room temperature and if no solid has separated add 1 to 2 ml. of N/10 sodium chloride. Allow

the reagent to stand for not less than twenty-four hours, and filter just before use, noting the temperature.

Procedure.—If a 2 ml. pipette is available, prepare a solution of sodium chloride by weighing accurately about 1·5 gram of the ignited salt, dissolving in water, and making up to 100 ml. Measure out 2 ml. of this solution into a small beaker for each determination. Otherwise weigh out 0·03 gram of sodium chloride into a small beaker, and add 2 ml. of water. In either case add 20 ml. of the filtered reagent, stir the mixture for several minutes, and allow it to stand for not less than half an hour at a temperature as near as possible to that at which the reagent was filtered. Filter the crystalline precipitate on a Gooch or No. 4 sintered glass crucible. Transfer the precipitate with small quantities of the reagent with the help of a rubber-tipped glass rod, and wash it in the crucible five times with 2 ml. portions of 95 per cent. alcohol, using a small wash-bottle or pipette, and finally with a few millilitres of ether. Dry at 40° to 50°, cool, and weigh. One gram of the triple acetate contains 14·95 mgrm. of sodium.

Note.—Since the solubility of the triple acetate in 95 per cent. alcohol is very small, it is only necessary to saturate the alcohol used for washing with the triple acetate if less than 4 mgrm. of sodium is being determined.

Determination of Sodium as Sodium Sulphate

Dissolve about 0·4 gram of sodium chloride in a little water in a small weighed dish, preferably of platinum. Add 10 ml. of normal sulphuric acid, and carefully evaporate the solution, first on a water-bath, and then by means of a very small flame, until no further evolution of white fumes takes place. Now raise the temperature to the full heat of the Bunsen for a short while. Cool, and sprinkle a small quantity of solid ammonium carbonate over the salt to decompose any sodium bisulphate, and heat with the blowpipe for ten minutes. Cool in a desiccator, and weigh. Repeat the ignition until the weight is constant.

STRONTIUM

Forms in which Strontium is precipitated

Strontium Sulphate.—This is the best method for strontium, but barium, calcium, and lead must be absent.

Strontium Carbonate.—In the absence of other metals which form insoluble carbonates, strontium can also be satisfactorily determined by precipitation with ammonium carbonate. Strontium carbonate can be weighed as such, being less easily decomposed by heat than calcium carbonate.

Strontium Nitrate.—This salt is insoluble in nitric acid of greater specific gravity than 1·460, and strontium may be separated from calcium in this form.

Determination of Strontium as Sulphate

Procedure.—Weigh out accurately about 0·8 gram of crystalline strontium chloride, $SrCl_2, 6H_2O$, into a 400 ml. beaker, and dissolve it in 100 ml. of water. Add 15 ml. of dilute sulphuric acid, and 100 ml. of alcohol. Stir thoroughly, and allow the mixture to stand overnight. Filter on paper, and wash with a mixture of alcohol and water (55 ml. of 95 per cent. alcohol and 45 ml. of water), until all the sulphuric acid has been removed. Incinerate the paper in a platinum or porcelain crucible apart from the precipitate, since strontium sulphate is rather easily reduced to sulphide. Treat the ash from the paper with 2 or 3 drops of a mixture consisting of 1 ml. of alcohol and 2 drops of concentrated sulphuric acid. Warm very gently until the excess of sulphuric acid has volatilised. Add the precipitate and ignite at the full heat of the Bunsen burner, taking care to avoid access of reducing gases to the crucible (see p. 211). Weigh as $SrSO_4$.

If barium is present, this must first be separated as chromate as described on p. 283, but the precipitate, being contaminated with strontium, must be dissolved in dilute hydrochloric acid, and the barium again precipitated as before. The combined filtrates, after the addition of 5 ml. of dilute hydrochloric acid, are evaporated to half their bulk, and the strontium is precipitated as carbonate by ammonium carbonate after neutralisation with ammonia. The precipitate is filtered, dissolved in hydrochloric acid, and the strontium determined as sulphate as described above.

Determination of Strontium as Nitrate

Procedure.—Weigh out accurately about 0·2 gram of pure strontium chloride, $SrCl_2, CH_2O$, and dissolve it in exactly 10 ml. of water in a small dry beaker. Add 26 ml. of pure

fuming nitric acid (sp. gr. 1·520) drop by drop from a burette with continuous stirring. Allow to stand for three or four hours, and filter through a No. 4 sintered glass crucible. Transfer and wash the precipitate with nitric acid made by diluting the 1·520 sp. gr. acid with water in the proportion of 26 ml. of acid to 10 ml. of water. Dry at 130°, and weigh as $Sr(NO_3)_2$.

Separation from Calcium.—In using this method for the determination of strontium in the presence of calcium, it is important that the final concentration of the nitric acid during precipitation should not be greater than that given above, as calcium nitrate may be precipitated in more concentrated acid.

SULPHATE

A volumetric method for the determination of sulphate in ordinary concentrations is given on p. 185. For the determination of sulphate in water, see p. 470.

Sulphate is usually determined gravimetrically as barium sulphate. For details, see p. 235.

SULPHIDE

A volumetric method for the determination of hydrogen sulphide is described on p. 146. Many sulphides are readily decomposed by dilute acids, and the volumetric method may therefore be adapted to their determination.

In order to determine sulphide gravimetrically, a weighed sample (or measured volume) is decomposed with hydrochloric acid in an apparatus similar to that shown in Fig. 35, p. 150. To prevent liberation of sulphur by atmospheric oxidation, the apparatus must be filled with carbon dioxide or hydrogen. The hydrogen sulphide is led into a solution of ammonia and hydrogen peroxide, and is thereby oxidised to sulphate. The sulphate is determined in the usual manner as barium sulphate.

The oxidation of the hydrogen sulphide may also be effected by absorbing the gas in sodium hydroxide solution, and then adding bromine.

The determination of sulphur in mineral sulphides is described in connection with the analysis of Iron Pyrites (p. 396), Copper Pyrites (p. 398), and Zinc Blende (p. 401).

TIN

Tin is a constituent of many alloys, such as solder, type metal, bearing (anti-friction) metal, bronze, etc. Apart from its occurrence in alloys, it is rarely met with in analysis except as cassiterite, which is mainly stannic oxide.

The determination of tin is best accomplished by volumetric methods, which are far more reliable than any gravimetric methods. The latter are usually troublesome and are often inaccurate, more especially when the determination involves the separation of the tin from antimony, arsenic, lead, and copper, with which it is commonly associated. The volumetric method described on p. 154 is applicable to tin alloys and ores containing also antimony, arsenic, lead, and copper.

A concise account of the most reliable and rapid methods for the determination of tin in its ores and alloys is given in Parry's *The Assay of Tin and Antimony*.

Forms in which Tin is precipitated

Stannic Acid.—Tin may be precipitated in this form either from a solution containing a stannic salt only, or by the disintegration of an alloy by nitric acid. The insoluble stannic acid is then ignited and weighed as stannic oxide. The oxide, however, retains appreciable amounts of the oxides of other constituents in the case of an alloy. If the amount of tin present in the alloy is less than 2 per cent., the error involved may usually be neglected; but if it exceeds 2 per cent. it is necessary to remove the tin, and determine the weight of the residual oxides by the method described below. An alternative procedure is given under the analysis of a fusible alloy on p. 373. Neither of these methods is applicable to alloys containing antimony, arsenic, phosphorus, or (in the case of the former method) bismuth.

Stannic Sulphide.—Tin is completely precipitated in this form by hydrogen sulphide in presence of hydrochloric acid the concentration of which is not higher than 2N. The precipitate may be oxidised by ignition in air and the stannic oxide weighed; or it may be dissolved in hydrochloric acid (with addition of potassium chlorate) and the tin in solution determined volumetrically.

Stannic sulphide is not precipitated from a solution containing 15 per cent. of hydrochloric acid (about 4N) or an excess of oxalic acid (contrast antimony sulphide, p. 280).

Determination of Tin as Stannic Oxide

A. In a solution of a Tin Salt.

Procedure.—Weigh out accurately about 0·2 gram of stannous chloride, $SnCl_2$, $2H_2O$, and dissolve in a mixture of 15 ml. of water and 10 ml. of dilute nitric acid in a 500 ml. beaker. Heat to boiling to oxidise the tin to the stannic state, and cool. Add 1 ml. of methyl orange, and run in dilute ammonia from a burette until the pink tinge has disappeared. Add 20 grams of pure ammonium nitrate, stir to dissolve, dilute to 250 ml., and heat to boiling. Allow the precipitate to settle, and filter. Wash with 2 per cent. ammonium nitrate solution, dry in a steam-oven, and ignite the precipitate in the filter in a porcelain crucible, and weigh as SnO_2.

B. In an Alloy.

OUTLINE OF METHOD.—The alloy is disintegrated with nitric acid, and the insoluble stannic oxide formed is filtered, washed, dried, and ignited. After weighing, the tin is volatilised by heating with ammonium iodide, and the weight of the residual impurities after reconversion to oxide deducted. Arsenic, antimony, bismuth, and phosphorus must be absent.

Procedure.—Weigh out accurately about 2 grams of a sample of bronze into a porcelain basin. Cover the basin, and add a mixture of 10 ml. of concentrated nitric acid and 3 ml. of water; warm on a steam-bath until the alloy is completely disintegrated. Rinse the cover-glass, and evaporate the solution on a water-bath until the residue is pasty. Add 5 ml. of concentrated nitric acid, and warm gently for several minutes. Add 30 ml. of water, and heat to boiling. Filter through paper, wash the precipitate with warm water containing nitric acid, and then with water alone. Dry the filter, and ignite it in a weighed porcelain crucible. Weigh after cooling. Now mix the residue intimately in the crucible with 15 times its weight of powdered ammonium iodide. Heat the crucible inside a larger one to a temperature [1] between 400° and 500° (just below dark red heat) until no more fumes are evolved.

[1] If iron is present the temperature must not rise above 475°.

Cool, add 2 to 3 ml. of concentrated nitric acid, and carefully evaporate to dryness on a hot plate. Decompose the nitrates by heating with a very small flame, and ignite at a low red heat to constant weight. The difference between this and the original weight gives the weight of pure stannic oxide obtained from the bronze. A sample of the ammonium iodide used should be tested in case any non-volatile impurity should be present.

TITANIUM

At one time regarded as a comparatively rare element, titanium is now recognised as one of the most widely distributed, and is more abundant in actual amount in the earth's crust than many more familiar elements such as tin, lead, carbon, and sulphur. It is probably an invariable constituent of all silicate rocks, although usually present to the extent of only 1 per cent. or less, but seldom merely as traces. It is also met with as an alloy in ferro-titanium, and is sometimes present in cast-iron and steel.

The colorimetric determination of traces of titanium is described on p. 259, and the use of a solution of titanous sulphate as a reducing agent in volumetric analysis has been described on pp. 160-162.

In the gravimetric determination of titanium it is often necessary to separate it from other elements with which it is associated. It is usually weighed as TiO_2 after precipitation in some other form which on ignition gives the oxide. Insoluble compounds of titanium, including the oxide, may be brought into solution by fusion with potassium pyrosulphate (p. 387), followed by extraction with dilute sulphuric acid.

Forms in which Titanium is precipitated

Meta-Titanic Acid, $TiO(OH)_2$, is precipitated by ammonia, and the precipitate is ignited to TiO_2 and weighed in the same manner as in the determination of iron as Fe_2O_3 (p. 225). In rock analysis the titanium will be precipitated together with hydroxides and phosphates of iron, aluminium, and manganese. The mixed precipitate, which after ignition contains titanium as TiO_2, is brought into solution after fusion with potassium pyrosulphate, and the titanium may be determined colorimetrically.

Titanium Oxinate, $TiO(OC_9H_6N)_2, 2H_2O$.—Titanium may be separated in this form under suitable conditions from alkali metals, alkaline earth metals, and magnesium.

Complex with Tannin and Phenazone.—By the use of these reagents titanium may be separated from the elements with which it is most commonly associated (iron, aluminium, and manganese), and also from silicon and phosphorus.

Determination of Titanium by precipitation with Tannin and Phenazone (Antipyrine)

OUTLINE OF METHOD.—The acidified titanium salt solution is precipitated by tannin and phenazone, and the precipitate is ignited and weighed as TiO_2.

Procedure.—A quantity of the sample, containing not more than 0·04 gram of titanium, is brought into solution if necessary by fusion with potassium pyrosulphate. To the solution in a 600 ml. beaker add ammonia until just alkaline, then 10 ml. of concentrated sulphuric acid, and 100 ml. of 4 per cent. tannin solution. Dilute to 400 ml., and add a 20 per cent. solution of phenazone in water while stirring until all the titanium has been precipitated as an orange-red flocculent precipitate. This is ascertained by allowing the precipitate to settle, and adding more phenazone solution, when if no titanium remains, a white precipitate is produced with the excess of tannin present. Heat to boiling while stirring, and allow to cool. Filter on paper, with the aid of gentle suction (p. 36), using if necessary two filters as the precipitate is very bulky. Wash with a solution containing 3 ml. of concentrated sulphuric acid, and 1 gram of phenazone in 100 ml. of water. Dry the precipitate, and ignite very carefully with the filter in a weighed dish, preferably of platinum, heating finally with a Méker burner until all the carbon is burned away. Weigh the residue of TiO_2.

TUNGSTEN

Tungsten is usually determined by a gravimetric method. It is weighed in the form of its trioxide after precipitation as a compound which gives this oxide upon ignition.

Forms in which Tungsten is precipitated

Tungstic Acid.—Tungsten is precipitated in this form in the determination of tungsten in steel (p. 377). Tungstic acid can also be precipitated from alkali tungstate solutions obtained after fusion with alkali hydroxide or carbonate.

Benzidine Tungstate.—Tungsten is precipitated as benzidine tungstate by the addition of benzidine hydrochloride more completely than it is by evaporation with acid to form tungstic acid.

Mercurous Tungstate.—For this method phosphates, arsenates, chromates, molybdates, and vanadates must be absent.

Determination of Tungsten as Trioxide after precipitation as Benzidine Tungstate

OUTLINE OF METHOD.—Excess of benzidine hydrochloride solution is added to the tungstate solution in the presence of sulphuric acid, giving a mixture of benzidine tungstate and benzidine sulphate which is easier to filter than the former alone. On ignition tungsten trioxide only is left.

Tungsten Trioxide, WO_3, is a canary yellow solid, difficultly fusible, and not volatile at a bright red heat.

Procedure.—Grind 1 gram of benzidine with 40 ml. of 1 per cent. hydrochloric acid, transfer to a beaker, and wash out the mortar with another 10 ml. of 1 per cent. hydrochloric acid. Heat to dissolve the solid, and filter.

Weigh out accurately about 0·25 gram of sodium tungstate, dissolve in about 100 ml. of water, add 1 ml. of methyl orange, and make the solution just acid by the addition of decinormal sulphuric acid. Then add 10 ml. more of the acid, heat to boiling, and add 15 ml. of the benzidine hydrochloride solution. Stir for some minutes, allow the mixture to cool completely, and filter through ashless paper. Wash the precipitate with water containing about one-twenty-fifth of its volume of the benzidine reagent until the filtrate leaves no residue on evaporation. Ignite the moist precipitate with a Bunsen in a weighed porcelain crucible at the lowest temperature at which all organic matter and carbon can be burnt off. Weigh as tungsten trioxide.

Determination of Tungsten as Trioxide after precipitation as Mercurous Tungstate

OUTLINE OF METHOD.—Excess of a solution of mercurous nitrate is added to the solution of the tungstate in absence of chloride ions. The precipitate of mercurous tungstate is filtered off, washed, and ignited to tungsten trioxide.

Weigh out accurately about 0·25 gram of sodium tungstate, dissolve it in about 50 ml. of water, and make the solution *just* acid to methyl orange by the addition of nitric acid. Boil the solution to remove carbon dioxide, cool, and add a solution of mercurous nitrate (p. 476) until, after the precipitate has settled, it is found that no further precipitation occurs. Then add 3 ml. in excess. Stir the mixture, allow it to stand for four hours, filter through paper, and wash with a dilute solution of mercurous nitrate (1 part of the above reagent to 10 parts of water). Dry in a steam-oven, transfer to a weighed porcelain crucible, and ignite with a Bunsen burner *in a fume cupboard.* Weigh the residual oxide (WO_3) after cooling.

VANADIUM

Vanadium is determined both by gravimetric and by volumetric methods, the latter being generally more suitable. Volumetric methods depend on the reduction of pentavalent vanadium to the tetravalent condition and subsequent oxidation to the pentavalent state (p. 117). In the gravimetric determination vanadium is weighed as the pentoxide, V_2O_5, which, though easily fusible, does not volatilise on gentle ignition.

Forms in which Vanadium is precipitated

Mercurous Vanadate.—This method may be used for the determination of a vanadate after fusion with alkali. Phosphates, arsenates, chromates, molybdates, and tungstates must be absent.

Lead Vanadate.—The composition of this compound is not constant, and accurate results can only be obtained by the removal of the lead as sulphate or sulphide, evaporation of the filtrate, and ignition of the residue to vanadium pentoxide.

Determination of Vanadium as Oxide after precipitation as Mercurous Vanadate

OUTLINE OF METHOD.—The solution of an alkali or ammonium vanadate is precipitated by the addition of a solution of mercurous nitrate. The mercurous vanadate obtained is ignited to oxide and weighed.

Procedure.—Weigh out accurately about 0·2 gram of ammonium vanadate, and dissolve it in about 70 ml. of hot water. Cool, and add a solution of mercurous nitrate (p. 476) drop by drop from a burette until no further precipitate is produced, the precipitate being allowed to settle after each addition. Then add about 3 ml. in excess.

Boil the mixture, and, after the precipitate has settled, filter on paper, and wash the precipitate with a very dilute solution of mercurous nitrate (1 part of the above reagent to 10 parts of water). Dry the filter, ignite it *in a fume cupboard*, cool, and weigh the residue of vanadium pentoxide.

In the case of a vanadate obtained by fusion with sodium carbonate and potassium nitrate, the strongly alkaline solution must be almost neutralised with dilute nitric acid, excess being carefully avoided, since any nitrite formed during the fusion would liberate nitrous acid, with the subsequent reduction of vanadate to vanadyl salt which is not precipitated by mercurous nitrate.

WATER

Two methods, with many modifications of each, are used for the determination of water. The accuracy of the determination often depends on the choice of the appropriate method.

(1) **Indirect Method.**—A weighed sample is heated to a high temperature and the loss of weight is determined. This method is not always applicable.

(2) **Direct Method.**—A weighed sample is heated and the water evolved is collected and weighed. There are many modifications of the method of heating the substance and of collecting the water. The direct method is more generally applicable than the indirect method, but is somewhat more troublesome.

Indirect Determination of Water

As this is the easiest method, it is used whenever possible. It is inaccurate—

(1) If anything except water is lost during the dehydration. This is particularly liable to occur with carbonates, organic substances, and ammonium compounds.
(2) If the substance is readily oxidised. The method therefore gives inaccurate results if, for example, ferrous salts are present.

The first error can be avoided in some cases by dehydrating at a low temperature by means of a current of dry air or in a vacuum. The second error is avoided by dehydrating in an oxygen-free atmosphere or in a vacuum.

Three of the many modifications of the indirect method may be mentioned :—

(1) Gentle ignition until constant weight is attained. The procedure has already been described for the determination of water in magnesium sulphate heptahydrate (p. 222).

(2) Drying in a steam-oven or hot air-oven at constant temperature. Most hydrated salts can be dried at temperatures between 100° and 200° without further decomposition. There is no fixed temperature at which all hydrated salts will become anhydrous, and it is therefore necessary to ascertain for each substance the temperature, if any, at which the water can be expelled without further decomposition.

The substance is weighed in a wide, shallow weighing-bottle, and the open bottle is placed in the hot air-oven for one hour. The bottle is then removed and cooled in a desiccator. The stopper must be replaced before weighing, as re-absorption of moisture may occur. The procedure is repeated until the weight is constant.

(3) Most substances may be dried without decomposition in a vacuum desiccator containing sulphuric acid or fused calcium chloride. The substance should be weighed in a wide, shallow bottle or on a watch-glass. Dehydration may proceed so slowly at the ordinary temperature that it becomes complete only after many days ; if the substance is heated *in vacuo*, dehydration takes place very quickly and there is no risk of oxidation.

Direct Determination of Water in a Mineral

If the mineral on ignition loses only water and carbon dioxide, the following simple method (Brush and Penfield's) is convenient and accurate.

The mineral is heated in a hard-glass tube (about 20 cm. long and 5 mm. in diameter), which is enlarged into a bulb A (Fig. 68) at the closed end. One or more bulbs are provided near the middle of the tube in order to catch the water and prevent it running back and cracking the hot glass. A stopper C, for the open end of the tube, is made from a piece of tubing drawn out to a capillary and fitted with rubber tubing.

Even if apparently dry, these tubes must be thoroughly dried before use, by heating and blowing air through them by means of a narrow glass tube reaching to the bottom.

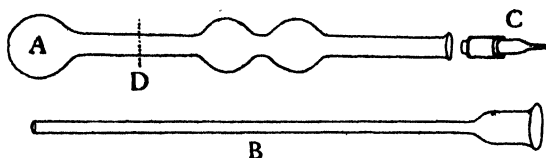



FIG. 68.

Procedure.—Weigh the empty bulb-tube. Introduce, by means of the tube B, from 0·5 to 1 gram of the substance, and weigh again. Insert the stopper C and clamp the tube in a horizontal position. Wrap strips of wet filter paper round the middle bulbs. Heat the bulb A, gently at first and then more strongly, with a Bunsen or a Méker burner, according to the temperature required to expel the water. It is advisable to protect the middle bulbs from the heat of the flame by means of a piece of asbestos board placed near the point D.

When the water has been completely expelled, draw off the heated end of the tube in a small blowpipe flame at the point D. Clean and dry the tube externally, cool for half an hour, and weigh it (without the stopper). Remove the water by warming the tube and aspirating air through it by means of tube B. Weigh the tube again after cooling.

If the substance contains sulphur, fluorine, etc., it must be mixed with some substance such as calcium oxide, to prevent the volatilisation of these elements.

Exercise.—Determine the percentage of water in gypsum or in barium chloride, heating with a Bunsen flame only.

ZINC

The volumetric method for the determination of zinc (p. 181) is more expeditious than the gravimetric methods, and is capable of yielding excellent results. The method requires practice, however.

Zinc is always determined after removal of the metals precipitated by hydrogen sulphide in acid solution. Zinc sulphide is partially precipitated with the sulphides of the copper group unless the solution is very strongly acid, and, in order to effect a complete separation, it may be necessary to redissolve the copper group precipitate, after filtration, and to reprecipitate with hydrogen sulphide.

Forms in which Zinc is precipitated

Basic Zinc Carbonate.—This method is applicable only when all metals other than sodium and potassium are absent. It is inaccurate in presence of ammonium salts, but these can be removed before precipitation. For details, see p. 233.

Zinc Ammonium Phosphate.—This method is available in presence of sodium, potassium, and ammonium salts only.

Zinc Sulphide.—Zinc may be separated from the calcium group by precipitation as sulphide, and in general analysis this is frequently the only available method. As, however, it is a matter of considerable difficulty to obtain zinc sulphide in a form suitable for filtration, it is preferable, when circumstances permit, to precipitate as basic carbonate or as phosphate.

A complete separation of zinc from iron, aluminium, manganese, cobalt, and nickel is obtained by precipitation as sulphide in presence of formic acid.

Zinc Oxinate.—By the use of this method zinc may also be determined volumetrically.

Metallic Zinc (Electrolytic).—See p. 249.

Determination of Zinc as Phosphate

OUTLINE OF METHOD.—The zinc is precipitated as zinc ammonium phosphate by means of ammonium phosphate in a very faintly acid solution. It is weighed either as $Zn(NH_4)PO_4$ after drying at 120°, or as $Zn_2P_2O_7$ after ignition.

Zinc Ammonium Phosphate is a white, crystalline powder, insoluble in water and in solutions of ammonium salts, but somewhat soluble in ammonia. It is readily soluble in mineral acids, but is almost insoluble in very dilute acetic acid. It may be dried without decomposition at temperatures not exceeding 140°; heated above 300°, it is converted into zinc pyrophosphate, $Zn_2P_2O_7$.

Zinc Pyrophosphate is a white powder which may be heated to dull redness without decomposition. Flame gases and carbonaceous matter must be carefully excluded during the ignition, otherwise reduction and volatilisation will occur.

Procedure (in absence of sodium and potassium).—The zinc solution should be just acid, and its volume should be about 100 ml. Add 6 to 10 times the theoretical amount of diammonium hydrogen phosphate, which has been dissolved in water and made just alkaline to phenolphthalein with dilute ammonia, and 3 grams of ammonium acetate. Heat on the steam-bath for an hour; in that time the precipitate should be crystalline and should have settled completely. Filter through a Gooch or sintered glass crucible, wash with hot water, dry at 110° to 120°, and weigh as $Zn(NH_4)PO_4$.

The above method is accurate, but if it is desired to weigh as pyrophosphate, the crucible must be placed inside a platinum or nickel crucible and ignited—at first gently, but finally to redness. Care must be taken to exclude flame gases during the ignition, since reduction (with volatilisation of the zinc) occurs readily.

Note.—The above mentioned conditions during the precipitation must be rigidly adhered to, or precipitation will be incomplete.

Modification if Alkalis are present.—If sodium or potassium salts are present, even in small amount, the precipitate obtained is a mixture of zinc ammonium phosphate and zinc potassium (or sodium) phosphate.

When these salts are present, add 20 grams of ammonium chloride to the solution, and precipitate as described above. When the precipitate has settled, decant through a Gooch crucible and wash three times with hot water by decantation, care being taken that as little as possible of the precipitate is washed into the crucible.

Dissolve the precipitate in the beaker in the minimum amount of dilute hydrochloric acid, add 10 grams of ammonium chloride, and repeat the process of neutralisation and precipitation. Filter through the crucible used in the first operation, wash thoroughly, ignite, and weigh as $Zn_2P_2O_7$.

It is necessary in this case to ignite to pyrophosphate, as in presence of large amounts of ammonium salts, the zinc ammonium phosphate is contaminated with ammonium salts which are not completely removed by washing.

If only sodium salts are present, a single precipitation in presence of a large amount of ammonium chloride is sufficient. The precipitate must be converted into pyrophosphate.

Determination of Zinc as Sulphide, after Precipitation in presence of Formic Acid

OUTLINE OF METHOD.—The zinc is precipitated as sulphide by hydrogen sulphide in presence of a small amount of formic acid. The sulphide is converted into oxide by ignition in air and the ZnO weighed; or it may be ignited in hydrogen and weighed as ZnS.

Zinc Sulphide, obtained by precipitation, is a hydrated, gelatinous substance. It is readily soluble in strong acids, insoluble in ammonia and in alkaline solutions generally, and almost insoluble in dilute solutions of acetic or formic acids. Whatever the conditions of precipitation, it is somewhat difficult to filter. The best precipitate is obtained from a slightly acid solution containing ammonium sulphate; it then filters fairly readily, but, if washed with water, becomes more gelatinous and chokes the filter paper. It can, however, be washed with dilute solutions of ammonium salts.

Zinc sulphide is quickly oxidised to zinc oxide on ignition in air, and is therefore usually converted into oxide for weighing; it can, however, be dried and obtained as anhydrous ZnS by gentle ignition with sulphur in an atmosphere of hydrogen, using a Rose crucible.

Zinc Oxide.—The properties of zinc oxide are described on p. 233.

Procedure.—To the zinc solution contained in a 400 ml. conical flask, add 1 ml. of methyl orange, and then run in carefully a dilute solution of sodium hydroxide until the last tinge of pink is discharged (avoid excess). Dilute 5 ml. of ordinary 95 per cent. formic acid to 100 ml., and add this to the zinc solution until a faint permanent pink colour is obtained, and then add an additional 5 ml. of the 5 per cent. formic acid, and 5 grams of ammonium sulphate.

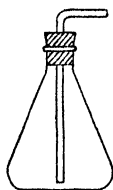



FIG. 69.

Dilute the solution to about 250 ml., heat to 80°, and saturate with hydrogen sulphide under slight pressure. Pressure a little above atmospheric is readily obtained with an ordinary Kipp apparatus if the flask is fitted with a rubber cork (Fig. 69). The cork is inserted firmly into place after the air in the flask has been displaced by hydrogen sulphide. When the solution is saturated and the precipitate has settled, the cork is removed before the apparatus is disconnected elsewhere.

Decant, filter with slight suction, and wash with a saturated hydrogen sulphide solution containing 2 per cent. of ammonium acetate ; wash finally with hot water.

Dry the precipitate and filter paper thoroughly. Remove the precipitate as completely as possible from the filter paper, but do not rub off any paper fluff, since this would cause reduction and loss of zinc in the subsequent ignition.

If the sulphide is to be weighed, incinerate the paper in a Rose crucible before adding the precipitate. Add a little pure sulphur, ignite at a low red heat in a current of hydrogen (see p. 214) and weigh the ZnS.

If the sulphide is to be converted into oxide, incinerate the paper before adding the precipitate, and ignite in an open crucible with careful exclusion of flame gases. Weigh the ZnO.

Determination of Zinc as Oxinate

The use of oxine as a reagent is described under Aluminium (p. 278).

Procedure.—To the solution containing not more than 0·06 gram of zinc add about 2 ml. of dilute hydrochloric acid and

25 ml. of 2N ammonium acetate. The final volume of the solution should be about 60 ml. Warm to about 60°, and run in from a burette 1 ml. of the oxine solution, prepared as described on p. 278, for every 4 mgrm. of zinc present. After mixing, the solution should have a yellow colour showing the presence of excess of the reagent. Heat nearly to boiling, filter through a No. 3 sintered glass crucible, wash with hot water (or, better, with a hot saturated solution of zinc oxinate), dry at 130°, and weigh as $Zn(OC_9H_6N)_2$.

Instead of drying and weighing the precipitate, it may be dissolved in warm 4N hydrochloric acid and aliquot parts titrated with a bromate-bromide mixture as described under Aluminium (p. 279). The volume of oxinate solution taken for titration should not contain more than 0·015 gram of zinc. One ml. of the standard bromate solution is equivalent to 0·817 mgrm. of zinc.

PART VI

THE ANALYSIS OF SIMPLE ORES AND ALLOYS

WHEN a complete analysis of a substance is made, as in some of the examples described in this section, the sum of the ascertained percentages of the various constituents would be 100·0, if there were no experimental errors. In actual practice, this summation may be considered satisfactory if it lies between 99·5 and 100·5, and the results of a complete analysis ought always to be tested in this way. A satisfactory summation is, however, no proof that the analysis is accurate, since a plus error in the percentage of one constituent may balance a minus error in that of another. A summation that falls short of 100 may be due to mechanical losses (spilling of drops, spirting, etc.), or to the slight solubility of precipitates, etc.; or it may indicate that the substance contains other undetermined constituents. Errors due to imperfect washing of precipitates, impurities in reagents, the action of solutions on glass, etc., may account for a summation exceeding 100.

Examples of typical analyses are given in the Appendix (p. 479). A full qualitative analysis of the material should be carried out before the quantitative work is begun, unless the constituents are already known.

ANALYSIS OF A SILVER COIN

(Alloy of Silver, Copper, and Nickel)

British silver coins minted prior to 1920 contained, as a rule, from 90 to 95 per cent. of silver, the remainder being copper. Silver coins were later made from an alloy of silver, copper, and nickel, and the following method of analysis is applicable to an alloy of these metals. (See note 2, p. 366.)

Outline of Method.—The coin is dissolved in nitric acid. The *silver* is precipitated as silver chloride which is separated by filtration, dried, and weighed. In the filtrate, the *copper* is precipitated as cupric sulphide which is dissolved in nitric acid, and titrated with sodium thiosulphate. After removal of copper, the *nickel* is determined by the dimethylglyoxime method.

Procedure.—Clean the coin with emery cloth, and cut it into pieces with shears. Place a weighed portion (0·8 gram) of the alloy in a 400 ml. beaker provided with a cover-glass. Add a mixture of 10 ml. of concentrated nitric acid and 5 ml. of water, and warm on a hot-plate or a steam-bath until solution is complete. Rinse and remove the cover-glass, and evaporate nearly to dryness on the steam-bath.

Silver.—Dilute the solution to about 100 ml., and determine the silver as silver chloride. Details of the procedure are given on pp. 230 and 345.

Copper.—Transfer the filtrate and washings from the silver chloride precipitation to a porcelain basin, and evaporate to dryness on the steam-bath. Add 10 ml. of concentrated sulphuric acid, and heat the basin on a sand-bath until white fumes of sulphuric acid are copiously evolved. (This operation is necessary in order to remove nitric acid.) Allow the basin to cool, add a little water cautiously, and warm until the copper and nickel sulphates are dissolved. Transfer the solution to a 300 ml. conical flask, dilute to 150 ml., and heat the solution nearly to the boiling-point. Pass a slow current of hydrogen sulphide through the hot solution until the precipitate is quite black and settles quickly, and the supernatant liquid is clear and colourless. The rate at which hydrogen sulphide is absorbed is greatly increased if the gas-inlet tube is expanded to a bulb which rests on the mouth of the flask when the tube dips into the liquid. The precipitation requires at least half an hour.

In the meanwhile, prepare some hydrogen sulphide solution by passing the gas into water contained in a special wash-bottle fitted for use with a valve (Fig. 17, p. 36).

When the precipitation is complete, remove the gas-delivery tube, and rinse it into the flask; rub off any adhering precipitate by means of a rubber-tipped glass rod, and rinse the tube again, internally as well as externally, and also the rod. Decant the liquid through a 9-cm. filter, and, with the help

of the hydrogen sulphide solution, transfer the precipitate at once to the filter. Wash the precipitate and filter, especially the margin of the latter, with hydrogen sulphide solution until the washings are no longer acid to litmus paper. During the whole process of filtration and washing, the precipitate must be kept covered with the washing liquid as far as possible to prevent partial oxidation and solution of the precipitate. Keep the filtrate and washings for the nickel determination.

Make a hole in the bottom of the filter with a drawn-out glass rod, and wash the precipitate into a conical flask. Pour hot nitric acid (1 of nitric acid with 2 of water) all round the top of the filter to dissolve the copper sulphide, and wash with water. Dry the filter and ignite it in a crucible, and set on one side. Boil the contents of the flask until brown fumes cease to be evolved. Cool, and filter from the sulphur into a 250 ml. graduated flask. Wash the filter, dry, and ignite it in the same crucible. Cool, add 0·5 ml. of concentrated nitric acid and 1 ml. of water, and carefully heat until the black residue has dissolved. Dilute, and filter through a small filter into the 250 ml. flask. Wash the crucible and filter into the flask, and make up to the mark. Determine the copper in 100 ml. of this solution by titration with standard thiosulphate as described on p. 143, taking care to remove nitrous acid before the titration.

Nickel.—Boil the filtrate from the copper sulphide precipitate to remove hydrogen sulphide, reducing the volume to below 200 ml. Transfer, after cooling, to a 250 ml. graduated flask, filtering if necessary; wash the beaker and filter also into the flask, and make up to the mark. Determine the nickel in 100 ml. by precipitating with dimethylglyoxime, after rendering almost neutral with ammonia (p. 327).

Notes.—(1) Silver coins often contain a trace of iron which may be determined (after removal of the copper) by following in detail the procedure given below for the determination of iron in German silver.

(2) At the present time, silver coins also contain a little zinc. For the analysis of such an alloy the procedure described for German silver must be followed, after the removal of silver as silver chloride.

ANALYSIS OF A GERMAN SILVER

(*Alloy of Copper, Nickel, Zinc, and traces of Iron*)

OUTLINE OF METHOD.—The alloy is dissolved in nitric acid, and the solution is evaporated with sulphuric acid until all the nitric acid is expelled. The *copper* is precipitated and weighed as cuprous thiocyanate, precipitation with hydrogen sulphide tending to carry down part of the zinc. *Iron* is removed by double precipitation with ammonia. *Nickel* is determined in the filtrate from the iron by means of dimethylglyoxime. *Zinc* is precipitated in the filtrate from the nickel as zinc ammonium phosphate.

Procedure.—Weigh about 0·4 gram of the alloy, and place it in a small porcelain basin covered with a clock-glass. Add 2 ml. of water, and 5 ml. of concentrated nitric acid; warm gently until the alloy is dissolved, adding a little more nitric acid if necessary. Rinse the cover-glass, and evaporate to dryness on the water-bath. Cool, add 2 ml. of concentrated sulphuric acid, and heat carefully on a sand-bath until copious white fumes are evolved. Allow to cool; cautiously add 40 ml. of water, and stir to dissolve the sulphates.

Copper.—Add ammonia until the solution is only slightly acid, precipitate and weigh the copper as cuprous thiocyanate as described on p. 301.

Iron.—Evaporate the filtrate from the cuprous thiocyanate to about 30 ml., and to the hot solution add concentrated nitric acid *drop by drop* until no more brown fumes are evolved. (These fumes are poisonous.) This process not only decomposes the thiocyanate, but also oxidises the iron. Add ammonia in slight excess, and heat. Filter through a small paper, wash the ferric hydroxide with a little hot water, and set the filtrate and washings aside. Dissolve the precipitate on the filter with about 10 ml. of hot dilute hydrochloric acid, receiving the solution in the beaker in which the precipitation of iron took place. Reprecipitate the ferric hydroxide with ammonia; filter through the same paper, and wash thoroughly with a 2 per cent. solution of ammonium nitrate. The precipitate may either be ignited and weighed as Fe_2O_3 (p. 225); or, if too small for this, may be dissolved in dilute hydrochloric acid, and the solution made up to a known volume and determined colorimetrically (p. 256).

Nickel.—Combine the two filtrates from the iron precipitations, make the solution only just acid with hydrochloric acid, and determine the nickel by means of dimethylglyoxime (p. 327).

Zinc.—To the filtrate from the nickel determination add 5 ml. of concentrated hydrochloric acid, and boil for fifteen to twenty minutes to remove alcohol and excess dimethylglyoxime. Determine the zinc as zinc ammonium phosphate (p. 360).

ANALYSIS OF SOLDER

Commercial solder consists essentially of lead and tin (from 30 to 60 per cent. of the latter), but it usually contains also from 1 to 3 per cent. of antimony. When such an alloy is disintegrated with nitric acid, the insoluble residue consists of stannic and antimonic acids, together with a small amount of lead oxide, the quantity of which may be diminished by using concentrated nitric acid for the disintegration. The analysis of solder by the first method described below is therefore inaccurate since the presence of antimony is ignored, but the method may be used for a pure lead-tin alloy without very serious error. The second method is capable of giving accurate results with any lead-tin-antimony alloy, such as type metal.

OUTLINE OF FIRST METHOD.—The alloy is disintegrated with nitric acid which dissolves the lead and converts the tin into insoluble stannic acid. The stannic acid is separated by filtration, ignited, and weighed as stannic oxide. The lead in solution is determined as chromate or sulphate.

Procedure.—Roll the alloy into a thin foil, or obtain filings by rubbing it on a clean, medium-cut file. Place a weighed portion (about 0·3 gram) in a porcelain basin, add 5 ml. of concentrated nitric acid, and cover the basin with a clock-glass. Heat gently until the alloy is completely disintegrated. If this process is very slow, a few drops of water may be added. Remove and rinse the cover-glass, and evaporate to dryness on the steam-bath. Add 5 ml. of dilute nitric acid and 20 ml. of water, and heat until boiling. Filter. Wash the stannic oxide with hot water containing a little nitric acid, and then thoroughly with water alone.

Dry the stannic oxide in the steam-oven. Incinerate the filter paper, together with the stannic oxide, in a porcelain crucible at as low a temperature as possible. When all the

carbon has been burnt off, allow the crucible to cool, and add several drops of concentrated nitric acid to oxidise any reduced oxide. Heat gently until dry, and then ignite with a Méker burner until of constant weight. In order to exclude flame gases during the ignition, it is advisable to support the crucible on an asbestos screen (p. 211).

The stannic oxide may contain antimony oxide. It always contains some lead oxide, but if the procedure has been carefully followed, the amount of occluded lead oxide will not usually exceed 1 milligram. If desired, the stannic and antimony oxides may be removed by volatilisation with ammonium iodide (p. 351), and the lead in the residue converted to lead nitrate and added to the filtrate.

Determine the lead (in the filtrate from the stannic oxide) as sulphate or as chromate (p. 309). If the chromate method is used, add about 10 grams of sodium acetate in order to replace the nitric acid by acetic acid.

OUTLINE OF SECOND METHOD.—One portion of the alloy is dissolved in hydrochloric acid and the solution is evaporated to dryness. The residue is extracted with alcohol and the *lead chloride*, which is insoluble in alcohol, is weighed. Another portion of the alloy is dissolved in hydrochloric acid (with careful exclusion of air) and the *tin* in solution is determined volumetrically by means of standard iodine. In a third portion the *antimony* is determined volumetrically by standard potassium permanganate or potassium bromate.

Lead.—In a small conical flask warm about 0·5 gram of the finely divided alloy on the steam-bath with 20 ml. of concentrated hydrochloric acid. If it dissolves very slowly, pass chlorine gas [1] through the hot liquid until solution is complete. Transfer the solution to a basin and evaporate on the steam-bath almost to dryness. Add 20 ml. of absolute alcohol and stir well. Filter through a Gooch or sintered glass crucible, and wash the lead chloride with absolute alcohol. In presence of antimony, it is better to use absolute alcohol through which hydrochloric acid gas has been passed for a short time. Dry the $PbCl_2$ in the steam-oven, and weigh.

Tin.—Fit a 200 ml. flask with a rubber stopper and delivery-tube bent so that it can dip into a beaker when the flask is

[1] The chlorine may be readily obtained by very gently warming a small quantity of potassium permanganate with concentrated hydrochloric acid in a small flask.

supported in a sloping position. Place 25 ml. of concentrated hydrochloric acid in the flask, together with about 1 gram of marble in order to displace the air by carbon dioxide. Introduce about 0·2 gram (accurately weighed) of the solder, and at once insert the stopper and delivery-tube. Warm the acid gently (but do not boil), the delivery-tube meanwhile dipping into water contained in a small beaker. (Care must be taken, by maintaining a steady flame, to prevent the water running back into the flask.) When the solder has completely dissolved, remove the beaker of water and substitute another beaker containing sodium carbonate solution. Allow the solution to cool. Cooling may be hastened by holding the flask under the tap—the delivery-tube remaining in the sodium carbonate solution during the process.

When the solution is cold, drop a small chip of marble into it, and add about 75 ml. of cold air-free water (water that has been recently boiled and rapidly cooled). Titrate the solution at once with decinormal iodine, using starch as indicator.

The iodine solution must be standardised by means of pure tin (0·15 gram), or with standard sodium arsenite (p. 142).

Antimony.—Disintegrate about 1 gram of the alloy by heating with 20 ml. of concentrated sulphuric acid as described on p. 115, and determine the antimony volumetrically with either standard potassium permanganate (p. 115), or standard potassium bromate (p. 164).

ANALYSIS OF BRASS

(Alloy of Copper and Zinc, with small quantities of Tin, Lead, and Iron)

OUTLINE OF METHOD.—In one portion of the alloy, dissolved in sulphuric acid and hydrogen peroxide, the *copper* is determined either volumetrically (p. 143), electrolytically (p. 245), or gravimetrically as cuprous thiocyanate. After removal of copper, the *iron* is determined gravimetrically or colorimetrically, after precipitation as ferric hydroxide. The *zinc* is determined as zinc ammonium phosphate.

Another (large) portion of the alloy is disintegrated with nitric acid. The *tin* is oxidised to stannic oxide which is weighed, and the *lead* in solution is determined as lead sulphate.

Copper.—In a small covered porcelain basin dissolve about 0·3 gram of the alloy (in the form of fine turnings) by warming

with a mixture of 20 ml. of 4N sulphuric acid and 15 ml. of "20-volume" hydrogen peroxide.[1] If necessary, more hydrogen peroxide may be added later. When solution is complete, rinse the cover-glass, and evaporate as far as possible on a water-bath to decompose the hydrogen peroxide. Dilute to about 80 ml. and allow to stand some hours. If any lead sulphate or stannic oxide has separated, filter through a small filter, and after washing with normal sulphuric acid, neglect the residue. Add ammonia to the solution until it is only slightly acid, and determine the copper as cuprous thiocyanate (p. 301).

Iron.—Determine the iron in the filtrate from the cuprous thiocyanate as described under the analysis of German Silver (p. 367).

Zinc.—Combine the two filtrates from the iron precipitations, and make the liquid slightly acid with dilute hydrochloric acid. Adjust the volume to about 100 ml. by evaporation or dilution, and determine the zinc as zinc ammonium phosphate (p. 360).

Tin and Lead.—Place 5 grams of the alloy in a porcelain basin provided with a cover-glass. Add a mixture of 15 ml. of concentrated nitric acid and 5 ml. of water, and warm on the steam-bath until the alloy is disintegrated. Rinse the cover-glass, and evaporate on the steam-bath until the residue is pasty. Add 5 ml. of concentrated nitric acid, stir, and warm gently for several minutes. Then add 50 ml. of water and heat until almost boiling. Filter through a small paper, wash with hot water containing a little nitric acid, and then with water alone. Dry, ignite, and weigh the stannic oxide (p. 368).

Transfer the filtrate to a porcelain basin, and add 8 ml. of concentrated sulphuric acid. Evaporate on the steam-bath as far as possible, and then on a sand-bath until copious fumes of sulphuric acid are evolved. Cool, add 100 ml. of water cautiously, and stir to dissolve the copper and zinc sulphates. Set aside for an hour. Filter through a Gooch or sintered glass crucible, wash with dilute (1 : 30 by volume) sulphuric acid, and then with alcohol. Dry, and weigh the lead sulphate (p. 310).

[1] By the use of these reagents instead of nitric acid, the evolution of acid fumes during the subsequent evaporation is avoided. Nitric acid, however, is preferable if much tin or nickel is present.

ANALYSIS OF A BRONZE

A bronze is an alloy consisting essentially of copper and tin, but usually containing also some zinc, together with traces of lead, nickel, and iron. Gun-metal is composed nominally of ninety parts of copper and ten parts of tin. English bronze coins contain about ninety-five parts of copper, four parts of tin and one part of zinc. The amount of lead in bronze coins rarely exceeds 0·1 per cent., but much larger proportions of lead are present in some varieties of bronze. Aluminium bronze usually consists of about ninety parts of copper and ten parts of aluminium, but may contain tin and other metals.

It is assumed that the alloy under analysis contains copper, tin, and zinc, with traces of iron and lead. The method described will therefore apply to most varieties of bronze, slight modifications being necessary when aluminium or nickel is present.

OUTLINE OF METHOD.—One portion of the alloy is disintegrated with nitric acid. The insoluble stannic acid is filtered and washed, dissolved in a mixture of concentrated sulphuric and hydrochloric acids, and the *tin* in solution determined volumetrically. In the filtrate from the stannic acid, the *lead* is determined as lead sulphate. Copper is then removed by electrolysis, or as cuprous thiocyanate, and the *iron* is determined gravimetrically or colorimetrically, after precipitation as ferric hydroxide. The *zinc* is determined as zinc ammonium phosphate.

Another portion of the alloy is dissolved in aqua regia and the *copper* in solution is determined volumetrically.

Tin.—Place 2 grams of the alloy in a porcelain basin provided with a cover-glass. Add a mixture of 10 ml. of concentrated nitric acid and 3 ml. of water, and warm on the steam-bath until the alloy is disintegrated. Rinse the cover-glass, and evaporate on the steam-bath until the residue is pasty. Add 5 ml. of concentrated nitric acid, and warm gently for several minutes. Then add 30 ml. of water, and heat until almost boiling. Filter through an untared Gooch crucible, and wash the stannic acid with warm water containing nitric acid, and then with water alone.

Transfer the stannic acid and the asbestos to a 400 ml. conical flask, using about 25 ml. of water. Add (cautiously) an equal volume of concentrated sulphuric acid, and boil for

two minutes. Take care to avoid "bumping." Then add 50 ml. of concentrated hydrochloric acid and boil for two minutes. (The stannic acid dissolves, although the presence of the asbestos obscures this.) Reduce the stannic salt with antimony powder and determine the tin by titration with decinormal iodine (p. 155).

Lead.—In the filtrate from the stannic acid, determine the lead as lead sulphate. The procedure is given under Brass (p. 370).

Removal of Copper.—Electrolyse the solution (after the removal of tin and lead), using either stationary electrodes (p. 245) or a rotating anode (p. 246). The weight of copper deposited may serve for a determination of the copper, but the result will be slightly low as part of the copper is retained by the stannic acid. The copper may also be removed by precipitation as cuprous thiocyanate (see p. 301).

Iron and Zinc.—Evaporate the solution (after removal of tin, lead, and copper) to about 20 ml., and determine the iron and zinc as described under Brass (p. 370).

Copper.—Dissolve 0·6 gram of the alloy by warming with a mixture of 6 ml. of concentrated hydrochloric acid and 2 ml. of concentrated nitric acid in a 200 ml. flask. Boil the solution and destroy nitrous acid (p. 144). Dilute with a little water, add ammonia until a precipitate forms, and then acidify with acetic acid. (The stannic acid precipitated by the ammonia does not wholly redissolve in the acetic acid.) Cool the solution and dilute to 100 ml. in a standard flask. Determine the copper in 25 ml. volumetrically (p. 144).

ANALYSIS OF A FUSIBLE ALLOY

(Alloy of Bismuth, Lead, Tin, and Cadmium)

The best-known fusible alloys are Newton's alloy (two parts of bismuth, five parts of lead, and three parts of tin), Rose's alloy (two parts of bismuth, one part of lead, and one part of tin), and Wood's alloy (four parts of bismuth, two parts of lead, one part of tin, and one part of cadmium). The method described below is applicable to any of these alloys.

OUTLINE OF METHOD.—The alloy is disintegrated with nitric acid.

The insoluble residue of impure stannic oxide is washed, dried, ignited, and weighed; it is then fused with sodium carbonate and sulphur. The soluble sodium thiostannate is removed by extraction with water. The insoluble residue of lead and bismuth sulphides is dissolved in dilute nitric acid. The bismuth is determined as basic nitrate, the lead as sulphate, and the necessary corrections for the amounts thus found applied to the tin, lead, and bismuth.

The filtrate contains bismuth, lead, and cadmium, as nitrates. After separation of the bismuth as oxynitrate, the lead is determined as sulphate. The cadmium is determined either electrolytically or by precipitation as sulphide.

Place a weighed portion (about 0·6 gram) of the finely-divided alloy in a covered porcelain basin, add 10 ml. of concentrated nitric acid, and heat gently until the alloy is disintegrated, adding a few drops of water if this process is very slow. When the reaction is complete, add about 30 ml. of water, and boil gently for a few minutes. Filter, and wash the insoluble residue, at first with hot, dilute nitric acid, and then thoroughly with hot water.

Analysis of the Insoluble Residue

Tin.—The insoluble residue consists of stannic oxide with traces of bismuth and lead oxides. Dry, ignite, and weigh the impure stannic oxide as described on p. 368. After weighing the oxide, transfer it to a small mortar, powder it, and mix it intimately with six times its weight of equal parts of pure sulphur and anhydrous sodium carbonate. Heat the mixture in a *covered* crucible, gently at first and then with a full Bunsen flame for five minutes. Allow the crucible to cool before removing the lid. Place the crucible in a beaker and boil with 100 ml. of water. The tin dissolves as sodium thiostannate and the lead and bismuth remain as insoluble sulphides. Filter, wash the residue, incinerate the filter, and repeat the fusion. (As a rule, a single fusion is insufficient to bring all the stannic oxide into solution.) Extract with water, filter through a Gooch or sintered glass crucible, and wash the insoluble residue of lead and bismuth sulphides. Then pour boiling dilute nitric acid through the filter until the residue has dissolved. (A trace of the lead sulphide may be converted into insoluble lead sulphate; in case this has happened, use the same crucible for the filtration of the lead sulphate at a later stage.) Evaporate

almost to dryness, dilute to about 20 ml. and add *very dilute* ammonia until the solution is only slightly acid. Filter, wash the basic bismuth nitrate with dilute ammonium nitrate solution, and convert it into oxide as described on p. 286. Weigh the Bi_2O_3. To the filtrate from the basic bismuth nitrate, add 1 ml. of concentrated sulphuric acid and evaporate until dense white fumes are evolved. Cool, add 30 ml. of water, and proceed with the determination of the lead as sulphate as described on p. 310.

Calculate the weight of PbO corresponding to the weight of $PbSO_4$ obtained. Subtract the weights of lead and bismuth oxides from that of the impure stannic oxide, in order to obtain the weight of pure stannic oxide.

Analysis of the Soluble Portion

Bismuth.—The bismuth may be separated as basic nitrate, as described on p. 286. The following modification of the procedure is preferable, as it avoids the large dilution.

Evaporate the filtrate and washings on the steam-bath until nearly all the liquid has disappeared. Add 20 ml. of water, stir thoroughly, and again evaporate. Add about 100 ml. of dilute (2 grams per litre) ammonium nitrate solution, and keep the mixture for an hour, with occasional vigorous stirring, before filtering. Wash the bismuth oxynitrate with dilute ammonium nitrate solution. Convert the bismuth oxynitrate into oxide, as described on p. 286, and weigh as Bi_2O_3. Add the weight of bismuth oxide found in the crude stannic oxide.

Lead.—To the filtrate from the bismuth oxynitrate, add 3 ml. of concentrated sulphuric acid, and evaporate until dense white fumes of sulphuric acid are evolved. Proceed as directed on p. 310, but wash carefully about eight times with dilute (about normal) sulphuric acid before washing with alcohol; reject the alcohol washings. Weigh the $PbSO_4$, and add the amount found in the analysis of the insoluble residue.

Cadmium.—Determine the cadmium in the filtrate either electrolytically, as described on p. 249, or by precipitation as sulphide and conversion into sulphate. (For details, see p. 288.)

ANALYSIS OF STEEL

Steel always contains a certain amount of carbon, manganese, phosphorus, silicon, and sulphur; and, for special purposes, varying amounts of other elements such as chromium, tungsten, molybdenum, vanadium, nickel, and cobalt. The estimation of certain of these constituents is described elsewhere; chromium, p. 116, manganese, p. 113, phosphorus, p. 97, and vanadium, p. 267.

Carbon.—The total carbon in steel is determined accurately by combustion of the metal in oxygen in a silica tube at a temperature of 1000°. The gases resulting from the combustion are passed over hot platinised asbestos, and then through "chromic acid mixture" to absorb sulphur dioxide. The carbon dioxide is taken up, after drying, by passing through weighed soda-lime or potash tubes. (For details of procedure, see Scott's *Standard Methods of Chemical Analysis*, or other comprehensive work.)

Silicon and Sulphur in Steel

OUTLINE OF METHOD.—The steel is dissolved in nitric acid containing a little hydrochloric acid and potassium chlorate, whereby the silicon is converted into silica, which is ignited and weighed as such. The sulphur is converted into sulphate, which is determined as barium sulphate.

Procedure.—Weigh accurately about 5 grams of the steel into a porcelain dish of about 15 cm. diameter, and add 1 gram of potassium chlorate. The latter assists in the oxidation and fixation of the sulphur as sulphate. Cover the dish with a clock-glass, add 50 ml. of concentrated nitric acid, and then not more than 3 ml. of concentrated hydrochloric acid. Warm the dish carefully *in a fume cupboard*, and stop heating as soon as the reaction commences. When the reaction has moderated, heat the dish on a steam-bath. If there is any metal undissolved after heating the covered dish for half an hour add another 3 ml. of concentrated hydrochloric acid, and continue the heating. When all the metal has dissolved, add 20 ml. of concentrated hydrochloric acid, and evaporate as far as possible on the steam-bath after rinsing and removing the clock-glass. Cool, add 50 ml. of concentrated hydrochloric acid, and again evaporate as far as possible to complete the removal of nitric acid. Towards the end of the evaporation stir continuously,

and in order to dehydrate the silica place the dish in an air-oven at 110° for one hour. Throughout the whole process contamination by sulphur dioxide from burning gas must be carefully avoided. Cool, and moisten the residue in the dish with 5 ml. of concentrated hydrochloric acid. After five minutes add 30 ml. of hot water, heat to dissolve the iron salts, and filter. Transfer all the residue from the dish to the filter, using a rubber-tipped[1] rod, by means of small quantities of 1 : 1 hydrochloric acid. Wash the filter with hot water until free from chloride. Keep the filtrate and washings for the sulphate determination. Partially dry the filter, ignite, and weigh the residue, using a platinum crucible. The impure silica is then volatilised with hydrofluoric acid and sulphuric acid as described on p. 343.

Pour the cold filtrate and washings into a litre measuring flask containing 90 ml. of concentrated ammonia and 200 ml. of water, shaking the flask continuously during the addition. Make up to the mark, mix thoroughly, and allow the ferric hydroxide to settle. Siphon off about 600 ml. of the supernatant liquid, and filter through a dry filter into a 500 ml. flask, rejecting the first few millilitres of the filtrate. Evaporate the measured filtrate, with the rinsing of the flask, to about 200 ml. on a steam-bath. Acidify the solution with dilute hydrochloric acid, and precipitate the sulphate in the boiling liquid with barium chloride in the usual manner.

Tungsten in Steel

OUTLINE OF METHOD.—The steel is dissolved in hydrochloric acid, the solution oxidised with nitric acid, and the tungstic acid formed is filtered off and weighed as tungstic oxide. This method is suitable for steels containing over 0·5 per cent. of tungsten.

Procedure.—Dissolve 2 grams of the sample in 40 ml. of concentrated hydrochloric acid in a 400 ml. beaker of tall form. Solution of the sample usually takes place slowly, and necessitates prolonged digestion just below the boiling-point. After complete solution, heat to boiling, and carefully oxidise with concentrated nitric acid, avoiding excess.[2] Evaporate to

[1] Black rubber must be used, as red rubber contains sulphides.

[2] To oxidise iron from the ferrous to the ferric state by means of concentrated nitric acid, add this *drop by drop* to the boiling solution until no further change in colour can be observed.

a paste on a water-bath, allowing no portion of the residue to become dry.

To the residue, add 150 ml. of 20 per cent. hydrochloric acid, boil for five minutes, and allow to stand for at least an hour. Filter through a paper-pulp filter, washing with hot 5 per cent. hydrochloric acid until free from iron, and finishing the washing with 2 per cent. ammonium nitrate solution.

Transfer the filter and precipitate to a platinum crucible, and ignite at a temperature not exceeding 850°, *i.e.* at a cherry-red heat. Cool, and treat the precipitate with hydrofluoric acid, together with a drop of sulphuric acid, evaporating carefully to dryness to remove silica, and avoiding any loss by spitting. Ignite to constant weight at a temperature not exceeding 850°.

The ignited tungstic oxide is usually contaminated with iron oxide, and with titania (if titanium is present in the steel). To determine these, fuse with 5 grams of sodium carbonate, and extract the fused mass with water. Filter through a Whatman's No. 40 11-cm. filter, wash well with hot water, dry, and ignite the insoluble residue in the platinum crucible previously used. Cool, and weigh. This weight deducted from that of the previous residue, gives the weight of tungstic oxide, WO_3, formed. From this calculate the percentage of tungsten in the steel.

Molybdenum in Steel

The following method is used for steels containing more than 0·75 per cent. of molybdenum, and is suitable when vanadium, chromium, and tungsten are also present.

OUTLINE OF METHOD.—The steel is dissolved in hydrochloric acid, and the solution oxidised. The molybdenum is precipitated as sulphide, which is ignited and fused with sodium carbonate. The molybdate formed is estimated as lead molybdate.

Procedure.—Dissolve 2 grams of the sample in 45 ml. of concentrated hydrochloric acid, add 3 ml. of concentrated nitric acid to effect oxidation, and evaporate to a paste. Take up with 40 ml. of 1 : 4 hydrochloric acid, boil for two minutes, and filter off the precipitated tungstic acid through a paper-pulp filter, washing well with hot 10 per cent. hydrochloric acid. Dilute to about 400 ml., neutralise with sodium hydroxide

solution, and just clear the solution by the careful addition of 25 per cent. sulphuric acid, avoiding an excess of more than two drops.

Bring the solution to boiling-point, and pass a rapid stream of hydrogen sulphide through the hot solution for half an hour, adding at the end of five minutes four drops of 25 per cent. sulphuric acid. Heat again to boiling, and filter through a Whatman's No. 40 11-cm. filter; wash well with 2 per cent. sulphuric acid saturated with hydrogen sulphide. Dry the filter and precipitate, and carefully burn off in a porcelain crucible at a low temperature. Brush the ignited precipitate into a platinum crucible, and fuse with sodium carbonate. Cool, extract with hot water, filter, and wash well.

To the filtrate, which now contains sodium molybdate, add 1 ml. of phenolphthalein solution, just acidify with hydrochloric acid, boil to remove carbon dioxide, and neutralise with sodium hydroxide solution. Now add 5 ml. of concentrated hydrochloric acid, boil, add 5 grams of ammonium chloride, and 50 ml. of a solution of ammonium acetate prepared by adding 33 per cent. acetic acid to ammonium hydroxide (sp. gr. 0·88) until the cold solution is very faintly acid to litmus.

Then, to the boiling solution, add 20 ml. of 4 per cent. lead acetate solution, boil for five minutes, and allow to stand in a warm place for fifteen minutes. Filter through a paper-pulp filter, and wash well with hot water containing 2 per cent. ammonium acetate to remove lead salts. Dry, ignite at a low temperature, and weigh as lead molybdate, $PbMoO_4$.

Nickel in Steel

OUTLINE OF METHOD.—The steel is dissolved in hydrochloric acid, and after oxidation of the iron to the ferric state, the nickel is precipitated by dimethylglyoxime in presence of tartaric acid, which prevents precipitation of the iron when the solution is subsequently neutralised.

Procedure.—Dissolve 1 gram of the steel in 15 ml. of concentrated hydrochloric acid and 10 ml. of water in a 350 ml. beaker. To the boiling solution add concentrated nitric acid drop by drop until no further change in colour takes place. Evaporate almost to dryness on the water-bath and take up in water, adding a few drops of dilute hydrochloric acid if necessary. Add 2 grams of tartaric acid dissolved in water,

and then dilute ammonia until the solution is neutral to litmus paper. Add 2 grams of sodium acetate, dilute to 100 ml., heat nearly to boiling and add a slight excess of a 1 per cent. alcoholic solution of dimethylglyoxime. (Approximately 6 ml. of a 1 per cent. solution of dimethylglyoxime should be added for each 1 per cent. of nickel present.)

After standing an hour or two (but not overnight) filter on a Gooch or sintered glass crucible. Wash thoroughly with hot water, dry at 120° for an hour, and weigh.

ANALYSIS OF A LIMESTONE OR DOLOMITE

Limestone consists essentially of calcium carbonate, but may contain also some magnesium carbonate. If the proportion of magnesium carbonate is considerable, the rock is called a dolomite. The usual minor constituents are iron, aluminium, silica (either free or combined), and sometimes traces of carbonaceous matter, phosphate, and manganese. A careful qualitive analysis must therefore precede the quantitative analysis.

In the following description of the analysis, it is assumed that a dolomite containing magnesium and calcium carbonates with small quantities of iron, aluminium, silica (or silicate), and phosphate is under examination. The results of the analysis of a rock are usually stated in terms of the constituent basic and acidic oxides, expressed as percentages. In dolomite, for example, the results are given in terms of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , CO_2 , P_2O_5 , and H_2O, and it is convenient to tabulate them in that order.

OUTLINE OF METHOD.—The silica and silicates are separated from the remainder of the rock by treatment with hydrochloric acid. The soluble and insoluble portions are examined separately.

In the soluble portion (1) *iron* and *aluminium*, together with any phosphate, are precipitated by ammonia; (2) in the filtrate, *calcium* is determined by precipitation as oxalate; (3) after removal of the calcium, *magnesium* is determined as phosphate or oxinate.

The insoluble residue, after ignition, may be reported simply as *silica and insoluble silicates*; or, after fusion with sodium carbonate, the silica may be separated, and a complete analysis made.

In separate portions of the original mineral, *carbonate*, *water*, and *phosphate* are determined.

Separation into Soluble and Insoluble Portions

Reduce about 10 grams of dolomite to a fine powder, and place the powder at once in a stoppered weighing-bottle. Take portions of this powder as required, the weight of each portion being found by difference.

Place a weighed portion (about 1·5 gram) in a porcelain basin, and cover the basin with a clock-glass to prevent loss during effervescence. Moisten the powder with a little water, and, by means of a small measuring cylinder, introduce through the spout of the basin 10 ml. of concentrated hydrochloric acid. When the action has almost ceased, rinse the cover-glass and the side of the basin with water, and boil for a few minutes. Again rinse the cover-glass and remove it. Evaporate to dryness—as far as possible on the steam-bath, and afterwards on a *gently heated* sand-bath.

Add 3 ml. of concentrated hydrochloric acid to the cold mass, and after about a minute dilute with about 10 ml. of water; warm the covered basin on the steam-bath. Filter through a 7-cm. or 9-cm. paper and receive the filtrate in a 250 ml. beaker. Add a few drops of dilute hydrochloric acid to the basin and carefully rinse the insoluble residue into the filter with a *fine* jet of hot water. Remove any traces of silica adhering to the basin or stirring-rod with a small piece of filter paper and drop this into the filter. Rinse the basin into the filter once more, and then wash the insoluble residue about ten times with small (2 ml.) portions of hot water. A few drops of the last washing should give no turbidity with silver nitrate. The insoluble residue consists of silica and insoluble silicates; the filtrate, which should not much exceed 50 ml. in volume, contains the metallic radicals as chlorides.

Analysis of the Soluble Portion

For the most exact work, the trace of silica present in the solution must be removed by a second evaporation to dryness (p. 343), but for all ordinary purposes this is unnecessary.

Iron and Aluminium.—Add 2 ml. of concentrated nitric acid in order to oxidise any ferrous salt and to form ammonium nitrate when ammonia is added. Heat until almost boiling and neutralise most of the acid by adding 3 ml. of concentrated ammonia diluted with 5 ml. of water. Then add dilute

ammonia gradually, until a faint ammoniacal odour persists after stirring and blowing away the ammonia vapour. (Much excess of ammonia must be avoided.) Boil for one minute. Filter, and wash three times with hot water, without necessarily bringing every trace of the precipitate on to the filter paper. Set the filtrate aside. The precipitate is mainly ferric and aluminium hydroxides (together with any phosphate), but contains also traces of calcium and magnesium salts which must be removed by reprecipitation. Dissolve the precipitate *at once* by pouring about 10 ml. of hot, dilute hydrochloric acid over the filter paper and receive the solution in the original beaker. Wash the paper a few times with hot water, and preserve it until required later. Precipitate the iron and aluminium in the filtrate as before. Filter through the same filter paper, combining the filtrate with that from the first precipitation, and wash thoroughly with a 2 per cent. solution of ammonium nitrate. Incinerate the filter paper together with the precipitate in a silica crucible without preliminary drying. Ignite the oxides in the open, slightly inclined crucible (to allow excess of air) with a Méker burner. Cool, and weigh the Fe_2O_3 and Al_2O_3.

The iron and aluminium in the mixed oxides are determined as follows:—Add to the crucible containing the ignited precipitate about 2 grams of potassium pyrosulphate. Heat gently over a small flame, and proceed with the fusion as described in detail on p. 387. When no more undissolved particles are visible, allow the crucible to cool, add 2 ml. of concentrated sulphuric acid, and melt the contents of the crucible again. After cooling, place the crucible in a beaker with 50 ml. of water and heat until solution is complete, except for a trace of silica. Remove the crucible and rinse it. Without filtering, and after cooling, determine the iron by means of decinormal permanganate after reduction by zinc amalgam (p. 126), or hydrogen sulphide (p. 127). Calculate the weight of ferric oxide in the mixed oxides. The difference between the weight of the mixed oxides and the weight of the ferric oxide gives the weight of the alumina.

If phosphate is present, it should be determined in a separate portion of the mineral (p. 384), and a correction applied to the alumina. Calculate the phosphate as P_2O_5, and subtract this from the weight of alumina as determined above.

Calcium.—To the combined filtrates add 1 ml. of methyl orange and sufficient hydrochloric acid to make the solution faintly acid. Evaporate to about 200 ml.

Heat the solution to the boiling-point in a 400 ml. beaker. Remove the flame and add a boiling solution of 3 grams of solid ammonium oxalate. Make the solution distinctly alkaline with ammonia, and boil gently until the precipitate becomes granular. Keep the mixture for one hour, decant the supernatant liquid through a filter, and wash three or four times with hot water, retaining the precipitate, as far as possible, in the beaker. Dissolve the impure calcium oxalate in hot, dilute nitric acid (3 ml. of concentrated acid mixed with 7 ml. of water), dilute the solution to about 200 ml., heat until boiling, and reprecipitate the calcium oxalate by adding about 2 ml. of ammonium oxalate solution and then ammonia, drop by drop, until the liquid is alkaline. Boil for a few minutes, and set the beaker aside for an hour. (If magnesium is present only in traces, one precipitation is sufficient.) Proceed according to the directions on p. 238 for the determination of calcium, filtering through the same filter as that used for the first precipitation. Combine the filtrates from the two precipitations.

Magnesium.—From the weight of calcium carbonate equivalent to the calcium oxide found, together with that of the other constituents determined, calculate the approximate magnesium oxide content, assuming that the remainder of the mineral consists of magnesium carbonate. As not more than 0·1 gram magnesium oxide should be used for the determination of magnesium, a part only of the filtrates and washings from the calcium oxalate precipitation will probably be required. If the magnesium oxide is about 20 per cent., make up the filtrates to 500 ml. in a graduated flask, and measure out 150 ml. by means of a 50 ml. pipette. If the approximate magnesium oxide content is less than 0·1 gram, use the whole of the combined filtrates.

Owing to the considerable concentration of ammonium salts present, it is necessary to remove these either by evaporation to dryness, followed by gentle ignition; or better, by the careful addition of 30 ml. concentrated nitric acid, and evaporation to dryness on a water-bath. During the evaporation the nitric acid decomposes all the ammonium salts, and in the early stages loss due to effervescence must be guarded against by

covering the dish with a clock-glass, which must be rinsed on removal. After the ammonium salts have been driven off or decomposed, cool, and dissolve the residue, after covering the dish, by warming with 5 ml. of concentrated hydrochloric acid diluted with 20 ml. of water. Filter off any insoluble residue, and wash the dish and filter. Add methyl red, dilute to 150 ml., and determine the magnesium by double precipitation as phosphate as described on p. 315.

The magnesium may also be determined in a suitable volume (about one-fifth) of the filtrate from calcium by precipitation as magnesium oxinate, without the previous removal of ammonium salts (see p. 316).

Analysis of the Insoluble Portion

Incinerate the filter, without preliminary drying, and ignite the insoluble residue in a platinum crucible, and weigh. If the insoluble portion amounts to less than 2 per cent., it is sufficient for most purposes to report the amount as " silica and insoluble silicates " ; if it exceeds that amount, analyse it according to the following scheme.

Silica.—To the insoluble residue add about six times its weight of anhydrous sodium carbonate, and proceed according to the directions given on p. 341 for the determination of silica in an insoluble silicate.

The filtrate from the silica may contain any of the constituents found in the soluble portion. It may be added to the main solution, or it may be analysed apart from, and in the same manner as, the main solution.

Determination of Other Constituents

Separate portions of the original mineral must be used for the determination of water, carbonate, and phosphate.

Water.—Determine the amount of water by Penfield's method, using about 2 grams of the mineral for the determination. (For details, see p. 358.)

Carbonate.—Determine the carbonate by the direct method (p. 289). Use about 1 gram of the dolomite for the determination.

Phosphate.—The amount present is often so small as to be negligible. If it is to be determined, 2 to 5 grams of the

dolomite should be decomposed with dilute nitric acid. After evaporation to dryness and removal of silica, the phosphate is determined in the soluble portion by the molybdate method (p. 328).

ANALYSIS OF AN INSOLUBLE SILICATE

(*Felspar, Clay, Mica, etc.*)

Most of the natural silicates, such as clay, felspar, garnet, and mica, are complex alumino-silicates. For example, orthoclase (potassium felspar) may be represented as $KAlSi_3O_8$; anorthite (calcium felspar) as $CaAl_2Si_2O_8$; albite as $NaAlSi_3O_8$; kaolinite as $H_4Al_2Si_2O_9$; and muscovite (common or potassium mica) as $H_2KAl_3(SiO_4)_3$. Pure forms of these minerals are, however, almost unknown; thus, although orthoclase has essentially the composition represented by $KAlSi_3O_8$, in almost all specimens it is found that the potassium is to some extent replaced by sodium, calcium, and magnesium, whilst the aluminium is usually partially replaced by iron. Titanium is almost invariably present, and sometimes manganese. The analysis of a silicate therefore involves, as a rule, the determination of silica, aluminium, iron, manganese, titanium, calcium, magnesium, sodium, potassium, and, in some cases, phosphate, carbonate, and water.

Full information on this important branch of analytical chemistry, with details for the analysis of more complex silicates, will be found in Hillebrand's *Analysis of Silicate and Carbonate Rocks*. The practical details of manipulation are minutely described in Washington's *Chemical Analysis of Rocks*.

OUTLINE OF METHOD.—A portion of the silicate is fused with sodium carbonate, and the fused mass is extracted with excess of acid. The insoluble residue is *silica*. The filtrate contains the iron, aluminium, manganese, titanium, calcium, and magnesium, which are determined as follows: *Iron*, *aluminium*, *manganese*, and *titanium* are precipitated by ammonia, the amount of iron in the mixed precipitate being determined volumetrically and the manganese and titanium colorimetrically. After removal of the iron, aluminium, manganese, and titanium, *calcium* is precipitated as oxalate. After removal of the calcium, *magnesium* is determined as phosphate.

Separate portions of the silicate are used for the determination of (1) *sodium* and *potassium* by the Lawrence Smith method; (2) *water*; (3) *carbonate*; and (4) *phosphate*.

Break the mineral into small pieces on a clean steel plate. Take about 10 grams of clean pieces of the mineral, and crush in a percussion mortar to a coarse powder. Then grind to a fine powder in an agate mortar. The whole analysis is facilitated by reducing the mineral to a fine powder, but only for the determination of the alkalis is it essential to grind to the finest possible powder. The various constituents of a rock often differ very much in hardness, and it is not permissible to reject the portion that offers most resistance to grinding, since this portion probably differs in composition from the remainder. When, therefore, *the whole* of the sample has been reduced to a fine powder, mix it thoroughly, place in a stoppered bottle, and use portions of this powder for each of the following analyses.

Determination of Silica, Iron, Aluminium, Manganese, Titanium, Calcium, and Magnesium

Fusion with Sodium Carbonate or Fusion Mixture.—Take a weighed portion (0·9 to 1·1 gram) of the powder, and fuse it with 6 grams of anhydrous sodium carbonate or fusion mixture. (For details of the procedure, see p. 341.)

Silica.—Details for the separation of the silica after the fusion are given on pp. 342 to 344.

Iron, Aluminium, Manganese, and Titanium.—Add to the filtrate from the silica about 5 ml. of concentrated hydrochloric acid—in order to provide sufficient ammonium chloride to prevent precipitation of magnesium when ammonia is added. Heat until almost boiling and neutralise most of the acid by adding 7 ml. of concentrated ammonia diluted with 7 ml. of water. Then add dilute ammonia, drop by drop, until a faint ammoniacal odour persists after stirring and blowing away the ammonia vapour. Boil for one minute. Following the procedure described under Dolomite (p. 381), filter and wash the precipitate (use an 11-cm. paper if necessary), dissolve at once in hot 2N hydrochloric acid, and reprecipitate with ammonia as before. Add a *small* quantity of well-washed paper-pulp (see p. 37), and boil for about a minute. (The paper-pulp facilitates the washing of the precipitate, its reoxidation during ignition, and especially its subsequent solution in fused pyrosulphate.) Filter and wash the precipitate with a 2 per cent. solution of ammonium nitrate until free from

chloride. Ignite with a Méker burner and weigh the mixture of Fe_2O_3, Al_2O_3, Mn_2O_3 and TiO_2 in the platinum crucible containing the non-volatile residue from the silica (see p. 343).

Add to the crucible containing the ignited precipitate about 10 grams of powdered potassium pyrosulphate (previously fused). Heat gently over a small flame until the salt is fused, and after any moisture has been driven off (about thirty minutes) gradually increase the temperature—care being taken to avoid boiling or spluttering—until white vapour of sulphur trioxide is slowly given off. Continue heating until the particles of precipitate have entirely disappeared, the temperature being gradually raised until, towards the end of the operation, the bottom of the crucible is at very faint redness. By removing the flame and allowing the crucible to cool somewhat, the fused mass becomes less opaque and it is possible to see in a good light whether all the precipitate has dissolved. When no more undissolved precipitate is visible, heat for a few minutes longer and then allow the crucible to cool.

Add 5 ml. of concentrated sulphuric acid and melt the contents of the crucible again. Cool, place the crucible with about 100 ml. of water in a beaker, and heat gently. When the crucible is free from adhering sulphate, remove and rinse it. If the fusion has been successful, only traces of silica remain undissolved. Filter through a small paper and wash the silica. Ignite and weigh the silica in a platinum crucible, correct it for impurity (p. 343), and add the amount to the weight of the main silica precipitate. After volatilising the silica, fuse the slight residue in the crucible with a small piece of pyrosulphate, and add this to the main solution for the determination of iron, aluminium, manganese, and titanium.

Manganese.—Make up the filtrate to 250 ml. in a graduated flask, and remove with a dry pipette exactly 50 ml. for the colorimetric determination of manganese as described on p. 264.

Iron.—Transfer the 200 ml. remaining in the graduated flask to a larger flask, washing into this both the pipette and the graduated flask. Reduce the iron to the ferrous state by means of hydrogen sulphide, and determine the iron volumetrically with potassium permanganate (p. 127).

Titanium.—Evaporate the titrated solution to about 150 ml. and transfer it to a 250 ml. graduated flask. Add 10 ml. of

hydrogen peroxide, and dilute to the graduation mark. Determine the titanium colorimetrically (p. 259).

Aluminium.—From the total weight of the ammonia precipitate deduct the weights of Fe_2O_3, TiO_2, and SiO_2 obtained as above. The weight of Al_2O_3 is thus found. (If phosphate is present, it is determined in a separate portion of the mineral (p. 391) and the corresponding weight of P_2O_5 is deducted from the weight of alumina.)

Calcium and Magnesium.—In the filtrate from the iron, etc., determine the calcium and magnesium as described under the analysis of Dolomite (p. 383).

Determination of Sodium, Potassium, and Lithium

(Lawrence Smith Method)

OUTLINE OF METHOD.—The silicate is decomposed by heating with ammonium chloride and calcium carbonate. The mass is extracted with water, and a solution of the chlorides of calcium, lithium, sodium, and potassium is obtained. The calcium is removed, partly as carbonate and the remainder as oxalate. The sodium, potassium, and lithium are then determined in the usual manner.

The ammonium chloride must be pure, and it is advisable to sublime a portion for the special purpose of this determination. The calcium carbonate must be specially purified. The purest obtainable calcium carbonate (or pure calcspar) is dissolved in hydrochloric acid contained in a porcelain basin. Excess of ammonia is added to the solution which is heated almost to the boiling-point, and a freshly prepared solution of pure ammonium carbonate is then added. The precipitate is collected in a Büchner funnel, washed *very thoroughly* with hot water, and dried. Even after this purification, it may still contain traces of alkalis, derived probably from the vessels employed. A " blank " experiment must therefore be carried out with the same quantities of the reagents and in the same manner as in the actual analysis, and the necessary correction applied in subsequent analyses. If the weight of alkali chloride from 0·5 gram of ammonium chloride and 4 grams of calcium carbonate exceeds 2 mgrms., further purification of the reagents is necessary.

For a successful determination of the alkalis, it is in most cases essential that the substance should be ground to the finest

possible powder. If the mineral contains much alumina, the powder must be passed through a 200-mesh sieve. When mica is present, it cannot be reduced to a very fine powder on account of its ready cleavage into plates and the flexibility of these plates ; mica, however, is more readily decomposed than most silicates, and less thorough grinding suffices for it.

A special finger-shaped platinum crucible is most suitable for the ignition, but an ordinary 30 ml. platinum crucible is quite satisfactory. Certain precautions are necessary to prevent loss of the alkali chlorides by volatilisation. The crucible, with a well-fitting lid, should be supported on a perforated asbestos screen (p. 211) so that the lowest third, but not more, can be heated to a red heat.

Decomposition of the Silicate.—Weigh, by difference, about 0·5 gram of the silicate into a platinum basin or a large agate mortar. Add 0·5 gram of ammonium chloride and mix the powders very thoroughly by gentle rubbing and stirring with a small agate pestle. Weigh approximately 4 grams of calcium carbonate, add most of this to the basin, and continue the stirring and rubbing until thorough mixing has resulted. Place the platinum crucible on a sheet of glazed paper and put into it sufficient calcium carbonate to cover the bottom in order to prevent adhesion of the mass after the ignition. With the aid of a small spatula, transfer the mixture very carefully from the basin to the crucible. "Rinse" the basin, and clean the spatula with the remainder of the calcium carbonate and add this, together with any powder that has fallen on the glazed paper, to the crucible.

Support the covered crucible in a hole of appropriate size cut in asbestos board, and heat with a small flame for about ten minutes. When the odour of ammonia is no longer perceptible, increase the flame until the lower part of the crucible is heated somewhat above dull redness, and continue the heating for about forty minutes. In the case of minerals rich in alumina, the temperature must finally be raised to a bright red heat for fifteen minutes.

Allow the crucible to cool. Add 3 ml. of water to slake the quicklime that has been formed and to disintegrate the mass. After a few minutes transfer the contents of the crucible to a porcelain basin, detach any adhering portions with a platinum spatula (or a glass rod), and rinse the crucible with about

50 ml. of hot water. Use a wash-bottle of resistant glass. Carefully break down any lumps with an agate pestle, and boil gently for a few minutes. Filter into a beaker of resistant glass, and wash the residue thoroughly with about 150 ml. of hot water. The solution contains all the alkali chloride, together with some calcium chloride.

Removal of Calcium.—To the hot solution add 10 ml. of ammonia, and about 2 grams of ammonium carbonate dissolved in cold water. Filter into a 15 cm. porcelain basin, and wash the calcium carbonate thoroughly with hot water. To recover adsorbed traces of alkali metals, dissolve this precipitate in the least possible amount of dilute hydrochloric acid. Dilute the solution, and reprecipitate the calcium carbonate. Filter, wash, and combine the filtrates. Evaporate the filtrates to about 50 ml., transfer to a platinum basin, and evaporate to complete dryness on the steam-bath. Heat the covered basin in an air-oven at 140° for an hour, and then expel ammonium salts by gentle ignition (see p. 339).

The residue still contains traces of calcium and possibly sulphate, which are removed as follows :—Dissolve the residue in 3 to 4 ml. of water ; add 1 drop of barium chloride, 1 ml. of ammonium carbonate, and a few drops of ammonium oxalate. Evaporate almost to dryness on the steam-bath. Add 3 to 4 ml. of water, filter through a small paper into a weighed platinum crucible, and wash the basin and the filter 6 to 8 times with warm water, using about 2 ml. at a time. Add a drop of hydrochloric acid to the crucible, evaporate to dryness, and expel ammonium salts by gentle ignition. Finally, heat the bottom of the crucible to very faint redness (barely visible in direct daylight), care being taken to avoid actual fusion of the alkali chlorides. Cool, and weigh.

Determination of Sodium, Potassium, and Lithium.—The weight of the residue gives the weight of the mixed sodium, potassium, and lithium chlorides. If lithium is present, this metal is first separated from sodium and potassium as described on p. 312. In the absence of lithium, the mixed chlorides of sodium and potassium are analysed as indicated on p. 338. For very accurate work, impurity derived from the reagents, glass vessels, etc., should be determined by carrying out a "blank" experiment. It may be assumed without serious error that the impurity consists of sodium chloride only.

Note.—If the mixed chlorides do not dissolve completely in water, collect the insoluble residue on a small filter paper, wash with hot water, ignite, and weigh. If the weight is less than 1 mgrm., subtract it from that of the mixed chlorides ; if more than 1 mgrm., reject the analysis.

Determination of Water, Carbonate, and Phosphate

Water and Carbonate.—Use separate portions of the powdered mineral for the determination of (1) water, as described on p. 358 ; and (2) carbonate, as described on p. 289. Many silicates contain no carbonate, but it is often found in clays.

Phosphate.—Weigh accurately about 1 gram of the powdered mineral into a small platinum basin. Add 10 ml. of water and mix thoroughly by stirring with a platinum wire. Then add 10 ml. of concentrated nitric acid and 5 ml. of hydrofluoric acid. Evaporate to dryness on the steam-bath. Add 5 ml. of nitric acid, evaporate again and repeat the evaporation with nitric acid two or three times in order to decompose fluorides. Heat the dry residue until it becomes brown, add 15 ml. of dilute nitric acid and boil gently for a few minutes in order to convert any meta- or pyrophosphate into orthophosphate. Filter, and wash with warm, dilute nitric acid. Determine the phosphate in the solution by the molybdate method (p. 328).

ANALYSIS OF A GLASS

Ordinary " soft " glass, used for bottles, window glass, etc., is essentially a sodium-calcium silicate ; in " hard " glass the sodium is replaced by potassium. Flint glass is a potassium-lead silicate. Pyrex glass contains about 12 per cent. of boric oxide, and Jena glass is a sodium-zinc borosilicate. Aluminium and traces of iron, manganese, and magnesium are present in most glasses. Oxides of cobalt, copper, iron, chromium and manganese are used in the preparation of coloured glasses. Bone ash, cryolite, or fluorspar is added to common glass in order to render it opaque.

The commonest constituents of glass are therefore silica, sodium, potassium, calcium, lead, and aluminium, with traces

of iron, manganese, and magnesium. The analysis of a glass is therefore carried out according to the procedure for an insoluble silicate, but when lead and manganese are present the method must be modified as follows :—

OUTLINE OF METHOD.—The glass is fused with sodium carbonate, and the fused mass is extracted with hydrochloric acid. *Silica* is determined in the insoluble residue. In the filtrate from the silica, the *lead* is precipitated as sulphide. After removal of lead, the *iron*, *aluminium*, and *manganese* are precipitated together by means of ammonia and ammonium persulphate and weighed as oxides; the iron in the mixed oxides is determined volumetrically. After removal of iron, aluminium, and manganese, *calcium* is precipitated as oxalate and *magnesium* as phosphate.

Separate portions of the glass are used for the determination of (1) *manganese* by the bismuthate method, (2) *sodium* and *potassium* by the Lawrence Smith method, (3) hygroscopic *water*.

Fusion with Sodium Carbonate and Determination of Silica.—Fuse a weighed portion (about 1 gram) of the finely powdered glass with sodium carbonate, as described on p. 341. (If the glass contains lead, great care must be taken to maintain an oxidising atmosphere within the crucible, in order to avoid reduction of lead compounds and consequent serious damage to the crucible. The crucible must be placed on the triangle in a slightly inclined position so that the flame does not completely envelop it; and the sodium carbonate must be free from organic impurities, such as traces of paper and straw. A few centigrams of potassium nitrate may be mixed with the sodium carbonate in order to minimise the risk of reduction.) After dehydrating the silica, wash the insoluble residue with hot, dilute hydrochloric acid and then *very thoroughly* with hot water, since the lead chloride is somewhat difficult to remove. Test the purity of the silica in the usual manner, keeping the non-volatile residue.

Lead.—To the filtrate from the silica (about 150 ml.) contained in a 400 ml. conical flask, add moderately concentrated ammonia until a faint turbidity is obtained. Then add 5 ml. of concentrated hydrochloric acid. (In order to secure complete precipitation of the lead, the concentration of acid in the solution must not much exceed 0·3N.) Heat the solution to about 60° and saturate with hydrogen sulphide. Filter, and wash the precipitate with very dilute hydrochloric acid containing hydrogen sulphide. The precipitate, which may be light

brown in colour on account of admixed sulphur, invariably contains a trace of platinum sulphide derived from the crucible in which the fusion was made.

Dissolve the lead sulphide by pouring 20 ml. of boiling 5N hydrochloric acid into the filter in small portions, and receive the solution in a porcelain basin; wash the filter with hot water. Following the procedure described on p. 310, determine the lead in the solution as lead sulphate.

If only traces of lead are present, evaporate the lead chloride solution nearly to dryness, dilute to 100 ml. in a standard flask, and determine the lead colorimetrically (p. 262).

Iron, Aluminium, and Manganese

Evaporate the filtrate from the lead sulphide to 100 ml. and transfer it to a 250 ml. beaker. Add 3 ml. of concentrated nitric acid (to oxidise ferrous salt and to provide sufficient ammonium salt when ammonia is added) and heat until boiling. Remove the flame and neutralise most of the acid by adding 5 ml. of concentrated ammonia diluted with 5 ml. of water. Add 1 gram of ammonium persulphate, heat until boiling, and then add dilute ammonia until the solution is distinctly ammoniacal. Boil for not more than two minutes, and make sure that a faint ammoniacal odour persists.

Filter through a 9-cm. or 11-cm. paper (according to the amount of precipitate) and wash with a little hot water. Set the filtrate aside. Dissolve the precipitate in 10 to 20 ml. of hot 5N hydrochloric acid containing a few drops of sulphurous acid and receive the solution in the original beaker. Wash the filter paper. Reprecipitate with ammonia and ammonium persulphate, and add a small quantity of ashless paper pulp (p. 37). Filter, and wash thoroughly with hot water. Ignite the precipitate (with a Méker burner) in the platinum crucible containing the non-volatile residue from the silica (p. 392), and weigh the mixture of Fe_2O_3, Al_2O_3, Mn_3O_4, and a trace of SiO_2.

Iron.—Fuse the mixed oxides with potassium pyrosulphate as described on p. 387. Separate and weigh the silica that is always found here (see p. 387), and determine the iron volumetrically with centinormal permanganate, or colorimetrically. Calculate the percentage of Fe_2O_3 in the glass and also the weight of Fe_2O_3 in the ammonia precipitate.

Manganese.—Place a weighed portion (about 1 gram) of the finely powdered glass in a platinum basin. Add 10 ml. of sulphuric acid (1 : 1) and 5 ml. of hydrofluoric acid, and mix thoroughly by stirring with a stout platinum wire. Warm the mixture gently, with frequent stirring, to decompose the powder, and then evaporate as far as possible on the steam-bath. Remove the basin to a sand-bath and heat more strongly until fumes of sulphuric acid are evolved. Cool, add 3 ml. of concentrated sulphuric acid, dilute with a little water, and heat for a few minutes to dissolve soluble sulphates. Transfer the contents of the basin to a conical flask, dilute to 100 ml., and heat until almost boiling. (As a rule the sulphates dissolve completely—except possibly lead sulphate.) Cool to 40°, and determine the manganese in the solution by the bismuthate method as described on p. 114 for manganese in iron ore. The manganese may also be determined colorimetrically. Calculate the percentage of MnO in the glass, and also the weight of Mn_3O_4 in the ammonia precipitate.

Aluminium.—Deduct the weights of Fe_2O_3, Mn_3O_4, and SiO_2 (obtained as above) from the total weight of the ammonia precipitate. The weight of the Al_2O_3 in the precipitate is thus obtained and the percentage of Al_2O_3 in the glass may then be calculated.

Calcium and Magnesium.—In the filtrate from the iron, etc., determine the calcium and magnesium as described under the analysis of Dolomite (p. 383).

Sodium and Potassium.—In a separate portion of the glass (about 0·5 gram) determine the sodium and potassium by the Lawrence Smith method (p. 388).

Water.—Glass powder is very hygroscopic, and it is advisable to determine the "hygroscopic water" by Penfield's method (p. 358), and to express all other results as percentages of the dry glass. Analyses of the same sample made at different times will then be comparable.

ANALYSIS OF PORTLAND CEMENT

Portland cement is an instance of a silicate most of which can be decomposed by means of acid, rendering the process of fusion with carbonate unnecessary. The constituents are silica,

lime, alumina, and ferric oxide, with small amounts of oxides of alkali metals, magnesia, sulphur trioxide, and carbon dioxide. It may also contain traces of the oxides of titanium, manganese, and phosphorus, which are not usually determined separately.

OUTLINE OF METHOD.—The sample is decomposed by hydrochloric acid, and the silica rendered insoluble by evaporation and dehydration. The iron and aluminium (with any manganese, titanium and phosphate) are precipitated by ammonia, the amount of iron in the precipitate being determined volumetrically, and the aluminium calculated by difference. After the removal of these constituents, the calcium is precipitated as oxalate, and the magnesium subsequently determined as phosphate. Alkali metals are determined by the Lawrence Smith method on a separate portion of the sample. The sulphur trioxide is determined as barium sulphate on a further portion of the sample, which is also used for the determination of undecomposed constituents. The amounts of carbon dioxide and moisture are found by strong ignition of a larger portion of the sample.

Silica.—Weigh accurately between 0·5 and 0·6 gram of the sample into a porcelain dish, add 20 ml. of water, mix with a stirring-rod, and add 20 ml. of concentrated hydrochloric acid. Cover the dish, and heat on a water-bath until the cement is decomposed. Rinse the cover-glass, and continue the evaporation to dryness, stirring frequently towards the end. Dehydrate the silica, extract the basic constituents, and determine the amount of silica as described on pp. 342-344.

Iron and Aluminium.—In the filtrate from the silica, determine the iron and aluminium by double precipitation with ammonia as described under felspar (and, if necessary, manganese and titanium, p. 386).

Calcium.—In the combined filtrates from the iron and aluminium, determine the calcium by double precipitation as oxalate as described under Dolomite (p. 383).

Magnesium.—The magnesium in the whole of the combined filtrates from the calcium determination is precipitated as magnesium ammonium phosphate, and converted to magnesium pyrophosphate as described under Dolomite (p. 383).

Alkali Metals.—In a separate portion of the cement, in weight about 1 gram, determine the sodium and potassium by the Lawrence Smith method (p. 388).

Sulphur Trioxide, and Undecomposed Constituents.—Weigh accurately about 0·5 gram of the cement, and decompose

it with hydrochloric acid as described above. Evaporate the solution to dryness on the water-bath, and, without further dehydrating the silica, extract the basic constituents with hydrochloric acid, filter, and wash the silica. Keep the filtrate for the sulphur trioxide determination.

The silica is washed back into the dish used for the decomposition of the cement or (better) into a platinum dish, and enough sodium carbonate added to give approximately a 5 per cent. solution. The dish is then heated on a water-bath for about an hour to extract the free silica. Filter the solution, wash the undecomposed residue, ignite, and weigh.

The filtrate which has been kept for the sulphur trioxide determination is heated to boiling, and the sulphate precipitated by barium chloride solution as described on p. 235. In order to ascertain the amount of barium chloride required, assume that the cement contains about 3 per cent. of sulphur trioxide.

Loss on Ignition.—Weigh out about 1 gram of the sample, and heat strongly in a platinum crucible, which should be supported in a hole cut in an asbestos board. Cool, weigh, and repeat the ignition until the weight is constant.

ANALYSIS OF IRON PYRITES

Iron pyrites (pyrite) consists essentially of sulphide of iron, FeS_2, and in a good specimen the amount of other elements is very small. In many specimens, however, the iron is partially replaced by copper, and traces of arsenic, cobalt, and nickel are often present. Most specimens contain also a certain amount of "gangue"—consisting of enclosed or adhering particles of sand or other siliceous matter.

The analysis of iron pyrites therefore involves, as a rule, the determination of "gangue," copper, iron, and sulphur. It is sometimes necessary to determine also traces of arsenic, nickel, and cobalt, and the method described below must then be modified to include the determination of these elements.

Iron pyrites may be analysed by the method described on p. 398 for copper pyrites, but the following method is probably preferable.

OUTLINE OF METHOD.—The finely divided mineral is oxidised by means of sodium chlorate and hydrochloric acid. The *insoluble residue* is separated by filtration, ignited, and weighed. The *sulphur*, which has been completely oxidised to sulphate, is determined as follows:—The iron is precipitated by addition of ammonia, and, without filtering, the sulphate is precipitated as barium sulphate. The solution is then acidified with hydrochloric acid, in order to redissolve the ferric hydroxide, and the barium sulphate is collected and weighed.

The *copper* is precipitated from the filtrate as sulphide, and the *iron* is then determined either volumetrically or by precipitation as hydroxide.

Decomposition of the Pyrites.—Place about 0·3 gram of the *finely powdered* pyrites in a *dry*, 200 ml. conical flask, mix with 2 grams of powdered sodium chlorate, moisten with 3 ml. of water, and cool the flask and contents in ice. Add 20 ml. of concentrated hydrochloric acid, previously cooled in ice, and keep the flask in the ice for twenty to thirty minutes, with occasional *gentle* shaking. Remove the flask from the ice, so that the temperature will rise slowly. After about thirty minutes, warm the flask momentarily on the steam-bath, repeating this at intervals with gentle shaking, until the pyrites has entirely disappeared. The decomposition should proceed without the separation of sulphur, the oxidation of which, if it is in the form of lumps or liquid globules, is exceedingly tedious.

Transfer the solution, together with any insoluble gangue, to a porcelain basin, and evaporate to dryness on the steam-bath. Cover the dry residue with 5 ml. of concentrated hydrochloric acid, and, after five minutes, warm and add about 30 ml. of water. Filter into a 400 ml. beaker, and wash the residue with hot, dilute hydrochloric acid and then thoroughly with hot water. Incinerate the filter, ignite the residue strongly, and weigh. The residue consists, as a rule, of silica or insoluble silicates, and may usually be reported as "insoluble residue" or "gangue"; if, however, an analysis of it is required, proceed as directed on p. 344.

Sulphur.—Dilute the solution to about 200 ml. with cold water, and add ammonia in excess to the cold solution to precipitate the iron. Heat the solution until boiling, and precipitate the sulphate with a boiling solution of barium chloride, as described on p. 235. In order to estimate the quantity of reagent required, assume that the mineral is pure

pyrites, and use 5 per cent. more than the calculated amount, dissolved in 25 ml. of water.

Add dilute hydrochloric acid to the mixture in which the barium sulphate and ferric hydroxide are suspended, and, with frequent stirring, make sure that the latter has completely dissolved. (Avoid unnecessary excess of acid.) Cover the beaker and set it aside for at least six hours. The barium sulphate should appear perfectly white. Filter, wash, and weigh the barium sulphate.

Note.—The temporary removal of the iron from solution as ferric hydroxide is necessary in order to obtain the barium sulphate free from "occluded" ferric salts (see p. 235).

Copper.—In the filtrate from the barium sulphate, precipitate the copper as sulphide, dissolve and titrate as described on p. 365.

Iron.—After removal of the copper, determine the iron either (*a*) volumetrically, or (*b*) by precipitation as hydroxide.

(*a*) Ascertain that the iron is present entirely as *ferrous* chloride; if not, saturate the solution again with hydrogen sulphide. Expel the hydrogen sulphide with a current of carbon dioxide at the boiling-point, and cool. Titrate the solution with standard potassium dichromate, using diphenylamine as indicator (p. 120).

(*b*) Evaporate the solution in an open basin to expel hydrogen sulphide, oxidise with nitric acid, and proceed as described on p. 226.

ANALYSIS OF COPPER PYRITES

Copper pyrites (chalcopyrite) consists essentially of a copper-iron sulphide, $CuFeS_2$, and in a good specimen of the mineral the amount of other elements is negligibly small. Many specimens contain traces of silver, and more or less gangue is usually present.

The analysis of copper pyrites therefore presents a problem very similar to that of iron pyrites. The same methods are applicable to both, and copper pyrites may be analysed by the method described on p. 397, or, preferably, by the method described below.

OUTLINE OF METHOD.—In one portion of the mineral, the *sulphur* is oxidised by heating with sodium peroxide and sodium carbonate. The sulphate is then determined as barium sulphate.

Another portion of the mineral is decomposed with dilute nitric and sulphuric acids. The *insoluble residue* of silica, etc., is separated by filtration, ignited, and weighed. The *copper* in the solution is precipitated by means of aluminium and is collected on a Gooch or sintered glass filter, washed, dried, and weighed. The *iron* in the filtrate is determined volumetrically.

Determination of Sulphur

In a spun-iron crucible of about 30 ml. capacity mix 2 grams of dry sodium carbonate with 5 grams of sodium peroxide. Add a weighed quantity (about 0·3 gram) of the finely powdered pyrites and carefully mix the contents of the crucible by stirring gently with a nickel spatula or a glass rod. Place the crucible in a hole of appropriate size cut in asbestos board (Fig. 39, p. 211); heat very gently for about ten minutes, and then fuse the contents of the crucible by heating more strongly, but not above dull redness. Lift the asbestos board by opposite corners and rotate the crucible occasionally so as to rinse down the sides with the molten mixture.

Remove the flame, and, as soon as the contents of the crucible become solid, place the crucible upright in a 500 ml. beaker containing about 30 ml. of water. Cover the beaker and upset the crucible with a glass rod. Warm gently to dissolve sodium salts, and then remove the crucible and rinse it into the beaker. Add (cautiously) 8 ml. of concentrated hydrochloric acid to decompose some of the alkali hydroxide and carbonate. Filter through paper pulp (p. 37) and wash the precipitate thoroughly with hot water. Transfer the solution to a 500 ml. beaker, neutralise (approximately) by adding concentrated hydrochloric acid, and then add 1 ml. of acid in excess. Dilute the solution to about 250 ml., heat until boiling, and precipitate the sulphate with a boiling solution of barium chloride in slight excess (p. 236). Set aside for at least six hours. Filter (a Gooch or sintered glass crucible may be used), wash, and ignite the barium sulphate.

Determination of Copper and Iron

Place a weighed portion (about 0·4 gram) of the *finely powdered* pyrites in a porcelain basin or casserole provided with a cover-glass. Add 20 ml. of water, 5 ml. of concentrated nitric acid, and 5 ml. of concentrated sulphuric acid. Warm very cautiously, adjusting the heating so that there is a vigorous, but not turbulent, evolution of brown fumes. If this operation is properly conducted, there will be no residue of sulphur after about ten minutes' treatment; if any sulphur remains, continue to boil gently with occasional addition of a few drops of concentrated nitric acid. (If the sulphur collects into a single large bead, it may be removed from the solution by means of a glass rod, transferred to a crucible, dried, ignited, and any residue dissolved in nitric acid and returned to the main solution.)

When all the sulphur is oxidised, add a further 5 ml. of concentrated sulphuric acid, and evaporate on a sand-bath until copious white fumes of sulphuric acid are evolved; cool, and dilute the solution to about 40 ml. Heat the solution, and keep it hot until any anhydrous ferric sulphate has dissolved. Filter, wash with cold and then with hot water. Ignite and weigh the insoluble residue.

Copper.—Cut some sheet aluminium into pieces about 2 by 4 cm., and bend each piece at right angles across the middle. Place four of the pieces in the *hot* pyrites solution, cover the beaker, and heat gently on a hot-plate until the solution is colourless (about one hour). Cool the solution. Remove the aluminium with a glass rod and rinse the pieces carefully with a jet of water.[1] Collect the precipitated copper in a Gooch or sintered glass crucible, wash thoroughly with cold water and three times with acetone (reject the acetone washings), and dry in a steam-oven for twenty minutes. Cool, and weigh.

Iron.—Titrate the filtrate (without delay) with decinormal permanganate.

[1] Traces of copper may remain unprecipitated. If great accuracy is required, a solution of hydrogen sulphide should be added before filtering off the copper, and also used for washing the precipitate. In this case the copper and copper sulphide are dissolved in nitric acid, and a known fraction of the solution titrated with standard thiosulphate (p. 366).

Note.—If the aluminium contains a trace of iron—which is very probable—a correction for this impurity is necessary, and the above procedure must be modified as follows :—(1) Weigh (to the nearest centigram) the aluminium sheet before and after using it to precipitate the copper. (2) In another beaker mix 80 ml. of water and 10 ml. of concentrated sulphuric acid ; add a weighed quantity of aluminium (four pieces), and warm on the hot-plate beside the pyrites solution. After cooling, remove the aluminium, dry and weigh it. Titrate the solution with decinormal permanganate. (3) From the data obtained in (1) and (2) calculate the correction to be applied to the titration of the iron.

ANALYSIS OF ZINC BLENDE

Zinc blende consists essentially of zinc sulphide, but usually contains also traces of carbonate, cadmium, copper, lead, iron, and manganese. With most samples there is associated a certain amount of adhering siliceous matter.

OUTLINE OF METHOD.—One portion of the blende is decomposed with hydrochloric acid, and the *insoluble residue* is separated. *Lead* is determined in the filtrate as sulphate. After removal of lead, the *copper* is precipitated by means of hydrogen sulphide from a strongly acid solution ; the *cadmium* is then precipitated in a similar manner from a slightly acid solution. After removal of the copper and cadmium, the *iron* is precipitated by means of "cupferron," and the *manganese* is then separated as dioxide. In the filtrate, the *zinc* is determined as zinc ammonium phosphate, or volumetrically.

Sulphide and *carbonate* are determined in separate portions of the mineral.

One of the difficulties in this analysis is the separation of cadmium and zinc. The procedure given here is suitable for a zinc blende containing only a small quantity of cadmium.

Separation into Soluble and Insoluble Portions.—Introduce a weighed portion (1 to 1·5 grams) of the finely powdered zinc blende into a conical flask, and moisten the powder with water. Add about 20 ml. of concentrated hydrochloric acid, and close the flask loosely with a small funnel or glass bulb. Warm on the steam-bath until there is no further action, and then add from time to time a few drops of concentrated nitric acid. When the residue is white and when any sulphur has been brought into solution, add a further 10 ml. of concentrated hydrochloric acid,

and boil for five minutes. Filter the *hot* solution through a small filter paper and wash with a boiling solution of hydrochloric acid (half water and half concentrated acid) in order to dissolve any lead sulphate. Wash the residue with hot water, and ignite it. Weigh, and report the result as "insoluble residue."

Lead.—Evaporate the solution to about 10 ml., cool, add 3 ml. of concentrated sulphuric acid, and evaporate on a gently heated sand-bath until dense fumes of sulphuric acid are evolved. Cool, dilute to about 100 ml., and collect the precipitate of lead sulphate as described on p. 310. The precipitate must be thoroughly washed with dilute (normal) sulphuric acid before washing with alcohol. (Reject alcohol washings.)

Copper.—Evaporate the filtrate and washings from the lead sulphate until it begins to evolve fumes of sulphuric acid. Cool, add 20 ml. of water and 20 ml. of concentrated hydrochloric acid, and saturate the solution with hydrogen sulphide. Filter, and wash with a mixture of equal volumes of concentrated hydrochloric acid and saturated hydrogen sulphide solution, observing the precautions against oxidation mentioned on p. 365. Dissolve the cupric sulphide in nitric acid, and titrate a known fraction of the solution with standard thiosulphate (p. 143).

Cadmium.—Evaporate the filtrate until fumes of sulphuric acid appear. Cool, add 5 ml. of concentrated hydrochloric acid, and transfer the solution to a conical flask, using hydrogen sulphide solution to rinse the basin. Then add slowly, with constant stirring, hydrogen sulphide solution until the volume is increased to about 150 ml. Saturate the solution with hydrogen sulphide, collect the cadmium sulphide, and convert it into sulphate as described on p. 288.

Iron.—Evaporate the filtrate from the cadmium sulphide to about 50 ml. Transfer to a beaker, add 1 ml. of concentrated nitric acid, boil to oxidise ferrous salt, and dilute to 100 ml. Determine the iron by the "cupferron" method (p. 308), or by a double precipitation with ammonia as described on p. 367, adding in this case 2 grams of ammonium chloride before each precipitation.

Manganese.—In the filtrate from the iron precipitation, determine the manganese as described on p. 319.

Zinc.—After removal of manganese, determine the zinc as zinc ammonium phosphate (p. 360) or volumetrically (p. 181).

Sulphur.—Place a weighed portion (about 0·4 gram) of the *finely powdered* zinc blende in a 150 ml. conical flask. Add 20 ml. of a mixture of three parts concentrated nitric acid and one part concentrated hydrochloric acid, and immediately cool under the tap. After a few minutes, add two or three drops of bromine and warm very gently on the steam-bath until all the sulphur has been oxidised. Boil for five minutes, and then transfer to a porcelain basin, using concentrated hydrochloric acid to rinse the flask. Evaporate to dryness, add 5 ml. of concentrated hydrochloric acid, and again evaporate to dryness. To the residue add 30 ml. of water and 10 ml. of concentrated hydrochloric acid, and warm in order to dissolve any lead sulphate. Filter, and wash with a little hot, dilute hydrochloric acid and then thoroughly with hot water. Determine the sulphate in the filtrate as described on p. 235.

Carbonate.—In a separate portion (2 to 5 grams) of the zinc blende, determine the amount of carbonate (p. 289). Two U-tubes, each containing a concentrated solution of copper sulphate, must be placed next to the reaction flask in order to absorb the hydrogen sulphide.

ANALYSIS OF PYROLUSITE OR MANGANITE

Pyrolusite and manganite are the commonest ores of manganese. The former consists mainly of manganese dioxide, and the latter mainly of the hydrated oxide, Mn_2O_3, H_2O. Traces of "gangue," ferric oxide, and barium oxide are usually present in both minerals.

OUTLINE OF METHOD.—One portion of the mineral is extracted with hydrochloric acid, and the *insoluble residue* of silica, etc., separated. *Barium* is separated as barium sulphate, and the *iron* is then precipitated by means of "cupferron" or by the basic acetate method. After removal of iron, the *manganese* is determined as manganese dioxide.

In another portion of the mineral, the *manganese dioxide* is determined by a volumetric method.

Water is determined in a separate portion of the mineral.

Determination of Barium, Iron, and Manganese

To a weighed portion (about 0·5 gram) of the finely powdered mineral in a conical flask, add 10 ml. of water and 20 ml. of concentrated hydrochloric acid, and close the flask loosely

with a funnel or glass bulb in order to prevent loss by spurting. Warm on the steam-bath until the residue is white, and then evaporate to complete dryness in a porcelain basin. Moisten the dry residue with concentrated hydrochloric acid, set aside for five minutes, and then dilute to about 30 ml. Filter through a small filter paper; wash the residue, and ignite it. Weigh, and report the result as "insoluble residue."

Barium.—Heat the filtrate until boiling, and to the hot solution add 1 ml. of dilute sulphuric acid. Filter through a small filter paper, wash with hot water, incinerate the paper with the precipitate, and weigh the $BaSO_4$. The quantity of barium in these minerals is so small, as a rule, that the error due to the retention of ferric oxide by the barium sulphate is negligible.

Iron.—Precipitate the iron in the filtrate by means of "cupferron," as described on p. 308. The separation from manganese of the small quantity of iron in these minerals may also be effected by a double precipitation of the iron with the minimum excess of ammonia in presence of much ammonium chloride (*cf.* p. 367), or by the basic acetate method (p. 275).

Manganese.—After the removal of iron, precipitate the manganese, together with any traces of calcium, etc., as carbonate (p. 318). Filter, and wash thoroughly. Perforate the filter paper with a glass rod, and, by means of a jet of water, wash the precipitate into a beaker. Cover the beaker with a clock-glass, and dissolve the crude manganous carbonate in dilute sulphuric acid; wash the filter paper with a little warm, dilute sulphuric acid in order to dissolve any traces of precipitate adhering to it, and add these washings to the main solution. Dilute the solution to about 200 ml. and precipitate the manganese as dioxide (p. 319).

Manganese Dioxide.—In a separate portion of the mineral determine the manganese dioxide by either of the methods described under volumetric analysis (pp. 107 and 149). If the amount of manganese found in this way is less than the total manganese as determined gravimetrically, calculate the excess of manganese, above that present as the dioxide, as MnO.

Water.—Determine the water in the mineral by Brush and Penfield's method (p. 358).

ANALYSIS OF SUPERPHOSPHATE MANURE

Superphosphate manure is prepared from natural phosphate by treatment with sulphuric acid. By this treatment, insoluble tricalcium phosphate, $Ca_3(PO_4)_2$, is converted into soluble acid phosphate, $CaH_4(PO_4)_2$. The value of a superphosphate as a plant fertiliser depends mainly on the amount of soluble phosphate present. It is therefore often sufficient to determine only the respective amounts of "soluble" and "insoluble" phosphates. The following scheme for a more complete examination of a superphosphate is sufficiently comprehensive for most purposes.

OUTLINE OF METHOD.—Separate portions of the superphosphate are used for the determination of (1) "Siliceous matter," iron, aluminium, and calcium; (2) Soluble phosphate; (3) Total phosphate; (4) Sulphate; (5) Water, organic matter, sodium, and potassium.

The sample should be thoroughly mixed in order to secure uniformity, but it should not be dried or ground. All results should be expressed in percentages of the original, undried material.

Determination of Iron, Aluminium, and Calcium

Place about 2·5 grams (accurately weighed) of the superphosphate in a porcelain basin, add 20 ml. of water, 10 ml. of concentrated hydrochloric acid, and 1 ml. of concentrated nitric acid, and boil gently in the covered basin for about five minutes. Evaporate to dryness, first on the steam-bath and then on a *gently heated* sand-bath. Add 5 ml. of concentrated hydrochloric acid to the dry residue and warm gently; then add 30 ml. of water and heat for a few minutes. Filter, wash the insoluble residue with hot, dilute hydrochloric acid and then thoroughly with hot water. Ignite, and weigh the "insoluble residue."

Add sodium carbonate to the filtrate until it is alkaline (avoid loss due to effervescence), then add a few crystals of potassium nitrate and evaporate to dryness in a porcelain basin. Ignite the residue gently in order to destroy organic matter. Allow to cool. Dissolve the residue by warming with 10 ml. of concentrated hydrochloric acid diluted with 30 ml. of water. Transfer the solution (after filtering if necessary) to a 250 ml. standard flask, cool, and dilute to the mark.

Iron and Aluminium.—(*a*) Measure 50 ml. of the solution into a 600 ml. beaker, add 10 grams of ammonium chloride, 2 ml. of methyl orange, and ammonia until alkaline. Then add dilute hydrochloric acid, drop by drop, until just acid. Dilute to about 400 ml., heat until boiling, add 3 grams of ammonium acetate, and boil for two minutes. Filter, and wash with a little hot water. Dissolve the precipitate in hot, dilute hydrochloric acid, and receive the solution in the original beaker. Wash the filter paper. Add 10 grams of ammonium chloride to the solution, neutralise the excess of acid as before, dilute to 300 ml., and reprecipitate with ammonium acetate. Filter and wash with hot 2 per cent. ammonium acetate solution. Incinerate the paper, and ignite the precipitate in an open crucible with a Méker burner. Weigh the mixture of $FePO_4$ and $AlPO_4$.

(*b*) In another portion (100 ml.) of the solution determine the iron volumetrically. Reduce the ferric salt in a Jones reductor (p. 124) or with zinc amalgam (p. 126), or with stannous chloride (p. 128) and titrate with 0·02N dichromate (p. 118).

Calcium.—Mix the filtrates from the two precipitations of iron and aluminium phosphates and (without evaporation) precipitate the calcium as oxalate by adding 2 grams of ammonium oxalate (but no ammonia) to the boiling solution. Filter, wash the precipitate, convert it into CaO or $CaSO_4$, and weigh (p. 238).

Determination of Soluble and Total Phosphate

Soluble Phosphate.—Place 5 grams of the superphosphate in a 500 ml. measuring flask and add 400 ml. of water. Shake vigorously by means of a shaking machine for thirty minutes. Dilute the solution to 500 ml. and, after mixing, filter part of the turbid mixture. (Reject the first portion of the filtrate.) Determine the phosphate in 10 ml. of the filtrate (corresponding to 0·1 gram of the superphosphate) by the molybdate method, either gravimetrically (p. 328) or volumetrically (p. 96).

Total Phosphate.—Place a weighed portion (about 2 grams) of the superphosphate in a porcelain basin, add 25 ml. of water and 10 ml. of concentrated nitric acid, and boil gently in the covered basin for about five minutes. Evaporate to dryness,

first on the steam-bath, and then on a *gently* heated sand-bath. Add 5 ml. of concentrated nitric acid to the residue and warm gently; then add 30 ml. of water and heat for a few minutes. Filter, and wash the insoluble residue with hot, dilute nitric acid and then with hot water. Dilute the solution, after cooling, to 500 ml. in a standard flask. Determine the phosphate in 25 ml. of the solution by the molybdate method.

Insoluble Phosphate.—The difference between the total phosphate and the soluble phosphate (expressed as percentages of P_2O_5) gives the percentage of P_2O_5 present as insoluble phosphate.

Determination of Sulphate

Extract a weighed portion (0·5 to 1 gram) of the superphosphate with hydrochloric acid, evaporate to dryness, and prepare a solution as described on p. 405. In the filtrate from the insoluble residue, determine the sulphate as described on p. 235.

Determination of Water, Organic Matter, Sodium, and Potassium

Water.—Spread in a thin layer a weighed portion (2 to 5 grams) of the superphosphate in a platinum basin, and dry for five hours at 100°. Report the loss of weight as "moisture."

Place the dried sample in an air-oven, and dry at 160° to 170° until the weight is constant. Report the further loss of weight as "combined water."

Organic Matter.—To the dried residue, add saturated barium hydroxide solution, mixing thoroughly with a glass rod, until the solution is alkaline. Evaporate to dryness on the steam-bath, and dry at 160° to 170° until the weight is constant. Then heat on a sand-bath, gently at first, and finally for fifteen minutes to barely visible redness. Cool in a desiccator, and weigh. The loss of weight resulting from the ignition is the weight of the organic matter.

Sodium and Potassium.—If sodium and potassium are to be determined, it is convenient to use the residue after the above treatment. Proceed in the same manner as with the ignited mass obtained in the determination of the alkalis by the Lawrence Smith method (p. 389).

PART VII

GAS ANALYSIS

THE analysis of a gas is usually conducted in one or other of two ways.

(1) A measured volume of the gas is treated with a suitable absorbing-reagent and the change of volume noted, or

(2) A measured volume of the gas is treated with a suitable reagent, and the constituent thus absorbed is then determined in the reagent. This is the usual method for the determination of traces of one constituent, since large volumes of gas may be used; it is also the general method for gases that are readily soluble in water, such as sulphur dioxide.

In practice, gases are always measured in contact with mercury or water. The vapour pressure of mercury is so small at ordinary temperatures that it may be neglected except in the most exact work. The vapour pressure of water is much greater, and cannot be neglected in accurate work. As a rule, a gas is measured in the moist state at the room temperature and at barometric pressure, and corrections are then applied to find the volume the gas would occupy in the dry state at 0° and 760 mm. If v is the observed volume of the gas, t its temperature, p the barometric pressure in mm., and w the vapour pressure of water at temperature t, the corrected volume, V, is found from the following equation :—

$$V = v\,\frac{(p-w)\,273}{760\,(273+t)}.$$

Technical Methods.—Analyses can be performed rapidly and with sufficient accuracy for many purposes by using apparatus (designed mainly by Hempel) with water as the confining liquid. In these analyses the above-mentioned corrections are neglected, since the error introduced in this way is not larger than other errors inherent in the same methods. It is assumed, in fact, that the temperature and pressure remain

constant during the analysis. Any variation in the barometric pressure that may occur during an analysis is usually negligible, but care is necessary if the temperature variation is to be kept within sufficiently narrow limits. Obviously, the temperature will alter if any of the apparatus is brought near a flame, or is exposed to direct sunlight. For the same reason the apparatus must be lifted by the support, and the glass parts must not be touched more than is necessary with the hands.

COLLECTION OF A SAMPLE OF GAS FOR ANALYSIS

If a large quantity of the gas is available, it is most convenient to fill a tube or other vessel by displacement of the air originally present, care being taken that the air is completely displaced.

When the quantity of gas is limited, the receiver must be filled with water or mercury which is then displaced by the gas. An inverted wash-bottle with a piece of rubber tubing and a screw-clip on each of the tubes may be used for the collection of a gas (Fig. 70). In the laboratory it is usually possible to collect the gas directly in the gas-burette (see p. 412).

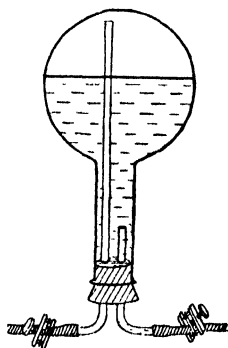



FIG. 70.

Samples of air in mines, etc., are conveniently collected in small (100 to 200 ml.) glass-stoppered bottles. To collect the sample, remove the stopper, insert a rubber cork fitted with inlet and outlet tubes, and blow the air through the bottle by means of a small bellows or other simple air-pump. Withdraw the rubber cork, and immediately insert the glass stopper which is lubricated with vaseline to render the bottle air-tight. Fix the stopper in position by means of a stout rubber band. The transference of the gas from the bottle to a gas-burette is described on p. 413. Instead of using a stoppered bottle, the sample may be collected in a glass tube with a tap at each end.

In connection with both the collection and the analysis of a gas, two points require special mention, viz., the solubility

of gases in water and aqueous solutions, and the permeability of rubber to gases. The solubility of nitrogen and oxygen is too small to affect an analysis seriously, particularly as the reagents are already saturated with these gases at their respective atmospheric partial pressures. With most other gases, the reagents should be saturated with each gas present in the mixture, at the pressure corresponding to its partial pressure. This is accomplished with sufficient exactness for most purposes by carrying out several successive analyses of the same sample; the error from this source will then diminish with each successive analysis, and the second or third analysis will be sufficiently accurate. Carbon dioxide, however, is so soluble that it cannot be accurately determined with any apparatus in which water is the confining liquid. Mercury is suitable for most gases which are soluble in water, but it cannot be used if chlorine, nitrogen peroxide, or hydrogen sulphide is present, as these gases react with the metal.

Since rubber is impermeable to water, one might presume that it would be impermeable to gases also, but this is by no means the case. All gases will pass through a rubber membrane even if it is free from flaws. The rate of diffusion through rubber varies with different gases, and is fast enough with carbon dioxide to introduce a serious error if the gas is exposed for any considerable time to a rubber wall. In practice, therefore, all rubber connections are kept as short as possible, and where practicable bound with wire. Old or parched rubber should never be used, and all rubber tubes should be tested for leaks from time to time. Clips of any kind should be removed when the apparatus is not in use.

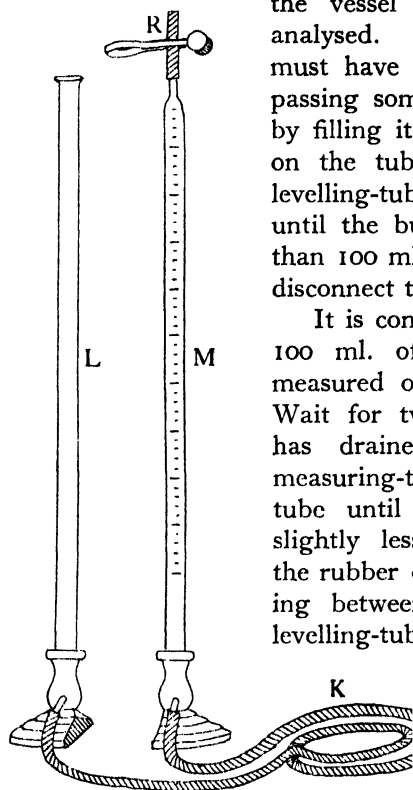
Gas Analysis with Hempel Apparatus

THE sample of gas to be analysed is introduced into a gas-burette, in which it is measured. It is then led into a gas-pipette, in which it is treated with a reagent which absorbs one constituent of the mixture. The residue is brought back into the gas-burette and the volume again measured, the contraction giving the volume of the constituent absorbed. The residue is then led into another gas-pipette, where it is treated with another reagent which absorbs a second constituent, and the residual gas is again brought back to the burette for measurement. This series of operations is continued, using as many pipettes as there are constituents to be determined.

THE GAS-BURETTE

This consists of a graduated measuring-tube M, and an ungraduated levelling-tube L (Fig. 71). Each tube is supported in an upright position by a stand, and the lower ends are connected by a rubber tube K of sufficient length to allow one tube to be placed on the floor while the other is on the working bench. The measuring-tube is graduated in fifths of a millilitre, from 0 to 100 ml. It terminates at the upper end in a short capillary tube to which a rubber tube R is attached. This rubber tube should be securely wired on to the glass capillary tube, leaving about 3 cm. of the rubber tube projecting.

To prepare the burette for an analysis, pour into the levelling-tube sufficient water to fill *one* of the glass tubes and the connecting rubber tube. In order to make sure that there is no air in the rubber tube, run the water to and fro in the tubes by alternately raising and lowering one of them. Then raise the levelling-tube until the measuring-tube and rubber tube R are completely filled with water, and close the rubber tube with a clip, placed as near the glass as possible.

Introduction of a Sample into the Burette.—Fill the measuring-tube with water as described above, and close the clip on the tube R. If the rubber tube R is not quite full, fill it from a wash-bottle. Insert into the rubber tube a well-fitting, capillary-bored, glass tube leading from the vessel containing the gas to be analysed. All air in the leading-tube must have been previously expelled by passing some of the gas through it, or by filling it with water. Open the clip on the tube R and, by lowering the levelling-tube, allow the gas to enter until the burette contains a little more than 100 ml. Close the clip on R, and disconnect the leading-tube.

It is convenient to work with exactly 100 ml. of gas, and this is readily measured off in the following manner. Wait for two minutes until the water has drained from the side of the measuring-tube, then raise the levelling-tube until the gas is compressed to slightly less than 100 ml. and close the rubber connecting-tube K by pinching between the fingers. Lower the levelling-tube and, by cautiously relaxing the pressure of the fingers on the tube K, allow the gas to expand until the volume is exactly 100 ml.; then pinch the rubber tube tightly again and open the clip on R for a moment. The excess of gas thereby escapes, leaving exactly 100 ml. at atmospheric pressure. Make sure that the volume is exactly 100 ml. by equalising the levels of the water in the two tubes of the burette and reading the volume of gas. When adjusting the water levels, hold the levelling-tube in a sloping position and bring it into contact with the measuring-tube. The measuring-tube must be vertical.

R L M K

FIG. 71.

The operation of introducing exactly 100 ml. of gas into the burette should be practised with air.

Introduction of a Sample from a Small Bottle.—Hold the mouth of the bottle below the surface of some mercury contained in a deep trough. Remove the stopper, care being taken that the mouth of the bottle is kept well below the

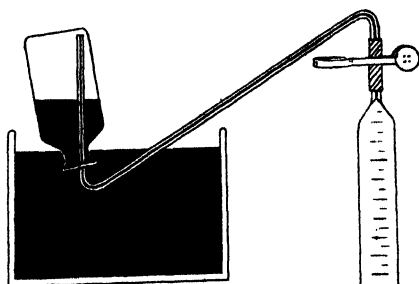



FIG. 72.

surface of the mercury. Fill a bent, thick-walled, capillary tube with water, insert it into the bottle, and connect the other end of the capillary tube with the gas-burette (Fig. 72). The burette may then be filled as described above.

ABSORPTION PIPETTES

Simple Absorption Pipette for Liquids.—This consists of two glass bulbs, A and B, connected by a wide tube. The bulb A is of about 150 ml. capacity and is connected with a long capillary tube C, which is bent as shown in Fig. 73. The bulb B must not be less than 120 ml. The pipette is supported on a suitable metal or wooden stand. A short piece of good rubber tubing is wired on to the open end of the capillary tube. When the pipette is not in use, this rubber tube should be closed with a glass plug, and the tube D should be closed with a small rubber stopper.

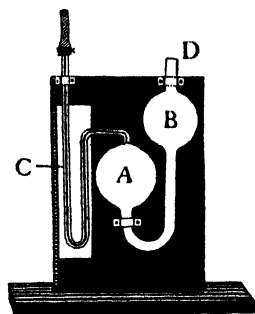



FIG. 73.

The pipette is filled by running in, through the tube D, sufficient of the reagent to fill the bulb A completely and the bulb B to a depth of about 1 cm.

Simple Absorption Pipette for Solids or Liquids.—This differs form the above form in having a tube at E (Fig. 74) through which a solid reagent may be introduced into the absorption bulb A. The tube E is closed with a rubber stopper which should be securely wired in place. With this pipette, absorption with liquid reagents can be greatly facilitated by packing the bulb A with rolls of wire gauze or with fine glass rods before filling the pipette with the reagent. When the gas is then introduced into A, it is exposed to a large surface of the reagent.

FIG. 74.

Double Absorption Pipettes.—Reagents, such as cuprous chloride, alkaline pyrogallate, etc., which absorb oxygen, must not be used in the simple pipettes described above. With these reagents, a so-called "double pipette" (Figs. 75 and 76) must be used. In this form of apparatus, the reagent in B comes into contact with an atmosphere free from oxygen, the indifferent gas being kept in place by water in the bulbs F and G.

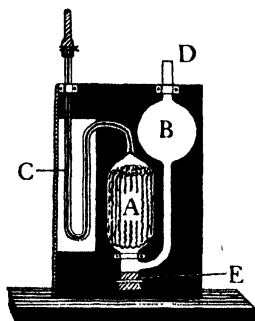
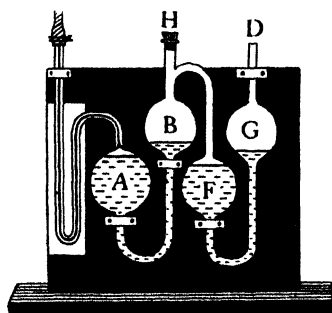
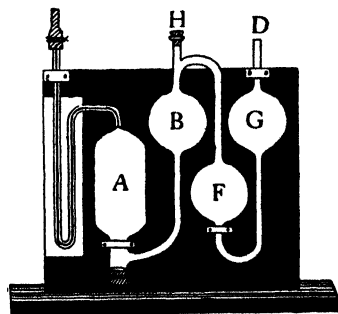



FIG. 75.

FIG. 76.

The filling of a Hempel double pipette, as ordinarily constructed, offers some little difficulty. By the addition of a

side-tube, shown in the diagram at H, the pipette is as easily filled as a simple pipette. The pipette is first filled with an indifferent gas, such as nitrogen or hydrogen, by passing it through while the tube H is closed with a cork. The reagent is introduced by pouring it in through the tube H, and water is poured in through D until the bulb F is almost full—in order to form a water-seal. The tube H is then closed with a well-fitting rubber cork.

MANIPULATION OF APPARATUS

Introduce the sample of gas into the burette in the manner already described. Clamp the burette to a pipette stand as shown at P in Fig. 77. Fill the rubber tube R with water and insert the capillary tube N as close to the clip as possible. (The tube N should become filled with water.) Blow through D by means of an attached rubber tube until the capillary C and the rubber tube S become filled with liquid; then insert N and push it down until the glass tubes touch within the rubber junction. (The capillary tubes N and C should now be almost, if not entirely, free from air; if an air column longer than 1 cm. is enclosed, the above operations must be repeated more carefully.)

Measure the volume of the gas sample contained in the burette—say v_1. Raise the levelling-tube, and open the clip on R *very cautiously* so that the gas enters the capillary N and drives the water over to a definite mark made on N just above the rubber tube S. Close the clip on R, equalise the levels, and read the burette again—say v_2. (The difference between v_1 and v_2, *i.e.* the volume of the capillary N, is usually about 0·2 ml.) Then raise L, open the clip on R, and drive the gas into the absorption pipette until water from the burette begins to flow into the bulb A by the capillary C, and close the clip on R. Bring the gas into intimate contact with the reagent by rocking the whole apparatus gently *backwards and forwards*. (This is unnecessary with a potassium hydroxide pipette containing wire gauze, or with a solid reagent such as phosphorus, on account of the large surface exposed to the gas.)

After rocking for five minutes, raise L and open the clip on R so as to rinse the end of the capillary C (where it joins A) with clean water from the burette. Lower L, the clip on R being

open, and bring the gas back into the burette until the reagent reaches the mark above the rubber tube S. Roughly equalise the levels, close the clip on R, and allow two minutes for the water to drain from the side of the burette. Equalise the levels and read the new volume of the gas. Repeat the operations—

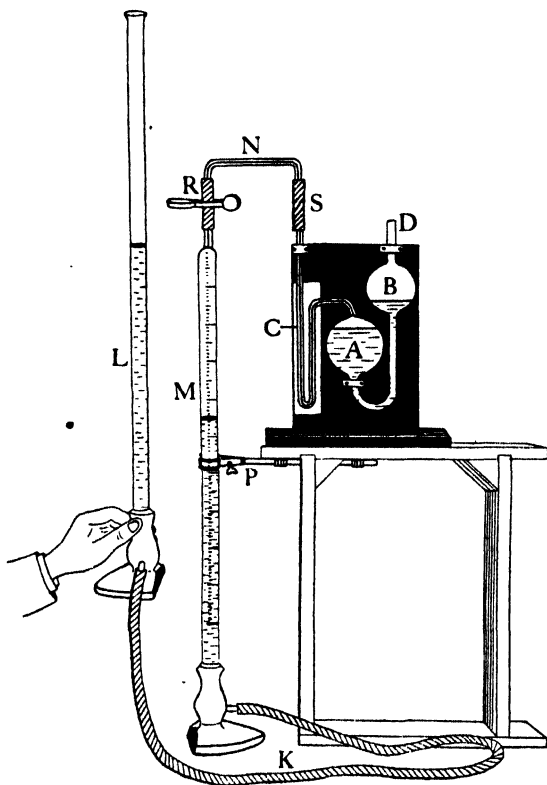



FIG. 77.

by passing the gas into the pipette again and back into the burette for measurement—until a constant value for the new volume (v_3) is obtained. Absorption is then complete. The final volume should not be read for five minutes, so that the temperature may become constant, and gas be resaturated with aqueous vapour. The difference between the second reading (v_2) and the last reading (v_3) gives the volume of gas absorbed; and if the original volume (v_1) of the gas was 100 ml., the

difference in millilitres is the percentage of the constituent in the mixture.

In order to determine the amount of a second constituent in the mixture, the original pipette with its rubber tube S is removed, the clip on R being, of course, closed; only a very small amount of reagent remains in the end of the tube N and serves to seal the capillary. A second pipette is then attached to N as before, and, the volume of the gas having been already measured to the mark on N, the absorption of the second constituent may be at once begun.

The final (true) volume of the residual gas may be found by adding the correction for the capillary N (usually about 0·2 ml.) to the volume last observed.

ANALYSIS OF A GASEOUS MIXTURE

In the analysis of a gaseous mixture, the gases must be determined in a definite order. The order in which the reagents *must* be used is given below for a mixture of the commoner gases; if a gas is known to be absent, the corresponding reagent will, of course, be omitted.

I. Potassium hydroxide . .	*for carbon dioxide.*
II. (*a*) Bromine; or (*b*) Fuming sulphuric acid (followed in either case by potassium hydroxide) . . .	*for ethylene, and other unsaturated hydrocarbons.*
III. (*a*) Sodium hyposulphite; or (*b*) Phosphorus; or (*c*) Alkaline pyrogallate; or (*d*) Chromous chloride . .	*for oxygen.*
IV. (*a*) Cuprous sulphate-β-naphthol, or (*b*) Ammoniacal cuprous chloride (followed by dilute sulphuric acid) . .	*for carbon monoxide.*
V. The unabsorbed residue is analysed as described on p. 421	*for methane, hydrogen, and nitrogen.*

REAGENTS USED IN ABSORPTION PIPETTES

Potassium Hydroxide. (*For carbon dioxide.*)—Dissolve 500 grams (or the contents of a 1-lb. bottle) in 1 litre of water and store in a bottle with a rubber stopper. Pack the absorption

bulb of a simple pipette (Fig. 74) with rolls of iron wire gauze of wide mesh and fill with the above solution of potassium hydroxide. When wet with this solution, the iron does not take up any oxygen by oxidation. Absorption of carbon dioxide in this pipette is usually complete in less than a minute.

One ml. of the reagent will effectively absorb about 40 ml. of carbon dioxide.

Sodium hydroxide must not be used instead of potassium hydroxide, as sodium bicarbonate is liable to crystallise out and block the capillary tube.

Bromine. (*For ethylene and other unsaturated hydrocarbons, and benzene.*)—Introduce into bulbs A and B of a double pipette (Fig. 75) the correct amount (as illustrated) of a saturated aqueous solution of bromine, and pour in a few millilitres of liquid bromine to ensure that the solution remains saturated. Pour water into F and G.

After the gas has been in contact with the reagent in the pipette for five minutes, draw it back into the burette, and then pass it into a potassium hydroxide pipette in order to remove bromine vapour; finally, return the gas to the burette, and measure it.

Fuming Sulphuric Acid. (*For ethylene and other unsaturated hydrocarbons, and benzene.*)—This reagent absorbs the same gases as bromine. A simple pipette, filled with glass beads or rods, may be used, but the special form with three bulbs, shown in Fig. 78, is recommended. The pipette is filled as usual, but great care must be taken that the reagent does not come into contact with the rubber connections or with water. The connecting-tubes must not be filled with water, and, when the gas is transferred to the pipette, care must be taken to prevent any water passing over into the pipette. The absorption is complete within five minutes. When the gas is withdrawn for measurement, allow the fuming sulphuric acid to follow until it reaches a mark made on the pipette capillary, showing the position of the reagent at the start of the experiment. (It is evident that an error is introduced on account of the air in the

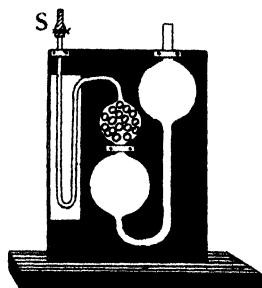
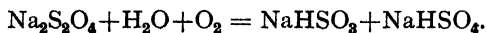



FIG. 78.

capillary. If the volume is known, a correction may be applied, but for many purposes the error is negligible; in any case the error affects only the oxygen and nitrogen determinations to any appreciable extent.) As fuming sulphuric acid has a high vapour pressure, acid vapour must then be removed from the gas by passing it into a potassium hydroxide pipette before measurement.

The pipette must be refilled after about 1 litre of ethylene has been absorbed.

Sodium Hyposulphite. (*For oxygen.*)—Dissolve 25 grams of sodium hyposulphite in 120 ml. of water and add 30 ml. of 50 per cent. sodium hydroxide. Introduce the solution at once into a double pipette. The reaction that occurs in the absorption of oxygen is represented by the equation

$$Na_2S_2O_4+H_2O+O_2 = NaHSO_3+NaHSO_4.$$

The absorption is complete within five minutes even at low temperatures, and is unaffected by ethylene, ammonia, etc. The pipette should be refilled after about 300 ml. of oxygen have been absorbed. The hyposulphite solution should be freshly prepared, as it does not keep.

Phosphorus. (*For oxygen.*)—The bulb of a simple pipette (Fig. 74) is packed with thin sticks of ordinary yellow phosphorus. The pipette is previously filled with water, and the bulb is covered with a metal cover to protect the phosphorus from the action of light.

Absorption of oxygen is marked by the appearance of white clouds of the oxide, and is complete within five minutes if the temperature is above 15°; at lower temperatures the absorption is much slower, and in cold weather sometimes does not occur at all unless the water in the pipette is warmed.

No absorption of oxygen takes place if the partial pressure of the oxygen is greater than about 0·5 atmosphere, or if the mixture contains ethylene, heavy hydrocarbons, ammonia, or alcohol, even in traces. If no white fumes appear, further treatment with bromine or fuming sulphuric acid should be carried out before oxygen is presumed absent. A mixture containing above 50 per cent. of oxygen may be diluted with a known volume of nitrogen, and the oxygen will then be absorbed.

Phosphorus is much cleaner to work with than alkaline

pyrogallate, and the pipette can be used for scores of analyses. The water must be changed from time to time. An error is liable to result from the use of phosphorus in the analysis of a gas mixture containing oxygen together with hydrogen or carbon monoxide, the latter gases being appreciably oxidised. In such cases one of the other absorbents should be used.

Alkaline Pyrogallate. (*For oxygen.*)—Dissolve separately 7 grams of pyrogallol in 25 ml. of water, and 50 grams of potassium hydroxide in 110 ml. of water. Mix the two solutions and introduce *at once* into a double pipette. Potassium hydroxide purified by alcohol must not be used.

The reagent absorbs oxygen very slowly at temperatures below 10°, but the absorption is rapid and complete at higher temperatures. The pipette must be refilled after about 200 ml. of oxygen have been absorbed, as carbon monoxide is liable to be evolved from a solution nearing exhaustion. The reagent will absorb oxygen in presence of ethylene, ammonia, and other substances that interfere with the absorption of oxygen by phosphorus ; but it should not be used for nearly pure oxygen, as carbon monoxide may be given off.

Chromous Chloride. (*For oxygen.*)—Transfer about 80 grams of chromic chloride to a stoppered bottle of about 400 ml. capacity. Add about 215 ml. of water, and 32 ml. of concentrated hydrochloric acid. Shake the contents of the bottle until the chromic chloride has dissolved. Add 300 grams of zinc amalgam (see p. 126), and shake vigorously until the solution becomes blue in colour, indicating that most of the chromic chloride has been reduced to the chromous state. The solution must be used in a double pipette.

Cuprous Sulphate-β-Naphthol. (*For carbon monoxide.*) —Cautiously add to 25 ml. of water, 200 ml. of concentrated sulphuric acid, and cool the mixture. In a mortar, rub 20 grams of cuprous oxide with the acid, adding later 25 grams of β-naphthol, until most of the solid has disappeared. Filter through glass wool, and transfer to a Hempel pipette. (The cuprous oxide is prepared by dissolving 100 grams of copper acetate in a litre of water, heating to boiling, and adding a solution of 60 grams of glucose and 50 grams of sodium hydroxide in 400 ml. of water. The liquid is boiled for a few minutes and filtered through a Büchner. The precipitate is washed with water and alcohol, and dried.)

This reagent, though rather slow in action, is better than cuprous chloride in ammonia, as it absorbs carbon monoxide completely, and does not absorb either hydrogen or methane as cuprous chloride is stated to do. The reagent will absorb more than five times its volume of carbon monoxide. Since traces of acid gases are liable to be produced, it is advisable to pass the gas into the potassium hydroxide pipette before final measurement.

Ammoniacal Cuprous Chloride. (*For carbon monoxide.*) —Dissolve 15 grams of cuprous chloride and 10 grams of ammonium chloride in the minimum quantity of concentrated ammonia solution, and dilute to 200 ml. Transfer the solution at once to a double pipette filled with rolls of copper gauze.

This reagent is used for the absorption of carbon monoxide, but, as it also absorbs carbon dioxide, oxygen, and ethylene, these gases must have been previously removed. Carbon monoxide forms with the reagent a compound having an appreciable dissociation pressure, and it is therefore necessary to pass the gas through two pipettes ; the first may contain a reagent that has been used several times, but the reagent in the second pipette should be as fresh as possible. The gas and the reagent *must* be brought into intimate contact by shaking (see below). Before measuring, the gas must be passed into a pipette filled with dilute sulphuric acid in order to remove the ammonia that escapes from the reagent.

Analysis of a Mixture of Methane, Hydrogen, and Nitrogen

OUTLINE OF METHOD.—After removal of all other gases, the methane and hydrogen are burned in a measured volume of oxygen. The products of combustion are removed, the contraction in volume is noted, and the amount of unused oxygen is determined. From the data obtained, the amounts of methane and hydrogen can be calculated. The residue is nitrogen.

Procedure.—Other gases are removed in the usual manner. The residue of methane, hydrogen, and nitrogen is transferred to a slow-combustion pipette (Fig. 79) in which the methane and hydrogen are burned by admitting a slow stream of oxygen, the necessary heat being supplied by an electrically heated platinum spiral. The spiral, which should be situated about 1 cm. from the top of the bulb, is heated to *dull redness* by

means of a current from a 4- or 6-volt accumulator. An adjustable resistance is required for regulating the current.

Pass the gas into the pipette and see that the capillary is completely filled with water. Close the rubber tube on the pipette with a screw-clip, disconnect from the burette, and connect with a second burette containing exactly 100 ml. of oxygen.[1]

After starting the heating current, raise the levelling-tube, place it on a tall stand, and open the screw-clip cautiously so that oxygen is driven *very slowly* into the pipette—at the rate of about 5 ml. per minute. (If the oxygen enters more rapidly, an explosion may occur.) During the combustion the spiral glows more brightly and the current must be regulated so that the wire is not heated much above dull redness. While combustion is in progress, the volume of gas in the pipette will contract; when combustion is complete the volume will steadily expand. After a decided excess of oxygen has been added, close the clip on the pipette and continue to heat the spiral for two or three minutes.

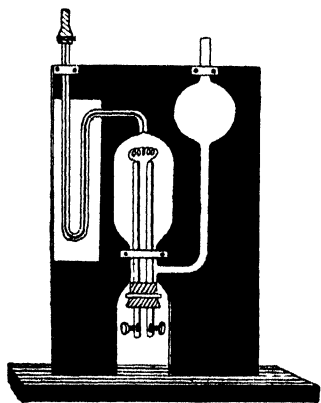
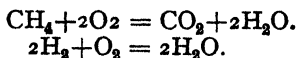



FIG. 79.

Pass the gas back into the original burette, and then, without previous measurement, into a potassium hydroxide pipette, in order to remove the carbon dioxide formed by the combustion of the methane. Return the gas to the burette and measure the volume. Absorb the excess of oxygen with phosphorus or sodium hyposulphite, and measure the residue.

The reactions that occur in the combustion are—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$
$$2H_2 + O_2 = 2H_2O.$$

If x be the volume of methane in the mixture, the volume of oxygen required for its combustion is $2x$; and if y be the

[1] For the preparation of pure oxygen, see Appendix, p. 477. For this experiment, the oxygen is collected in a gas-holder and stored till required. It should be analysed, and a correction applied if it contains any nitrogen.

volume of hydrogen, the volume of oxygen required for its combustion is $\frac{y}{2}$.

After combustion, the water and carbon dioxide are absorbed by the reagents. The contraction in volume resulting from the combustion of methane is three times the volume of the methane, *i.e.*, $3x$; and the contraction resulting from the combustion of hydrogen is one and a half times the volume of the hydrogen, *i.e.*, $\frac{3y}{2}$.

We have therefore :—

(1) The volume of oxygen used in the combustion $= 2x+\frac{y}{2}$.

(2) The contraction in volume on combustion $= 3x+\frac{3y}{2}$.

From these two equations, the quantities of methane and hydrogen are calculated.

The final unabsorbed residue is nitrogen, which, after correction for any nitrogen introduced with the oxygen, gives the quantity of nitrogen in the original mixture. This volume is, of course, the same as that obtained by subtracting the total of all the other constituents from the original volume.

There is no simple method for the direct determination of nitrogen.

Gas Analysis with the Orsat Apparatus

THE Orsat apparatus is a convenient, portable apparatus which is suitable for the analysis of flue gases, etc. The method of analysis is essentially the same as with the Hempel apparatus, but the burette, pipettes, and accessories are so modified that the whole apparatus, including three or four pipettes, will fit into a portable box. The number of pipettes or absorption vessels depends on the number of gases to be determined. The Orsat apparatus shown in Fig. 80 is designed for the determination of carbon dioxide, oxygen, carbon monoxide, and hydrogen.

The apparatus consists essentially of a measuring-tube *a*, provided with a water jacket to keep the temperature constant, and four pipettes *b*, *c*, *d*, and *h*.

The measuring-tube *a* has a capacity of 100 ml., with graduations at each $\frac{1}{5}$ ml. In order to economise space, the upper (40 ml.) portion of the tube is much wider than the lower portion. To the lower end is attached a stout rubber tube which leads to the levelling-bottle. The measuring-tube terminates at the upper end in a capillary tube which carries four side-tubes, with taps, leading to the four pipettes. The other end of the capillary tube is fitted with a three-way tap *k*.

Each pipette or absorption vessel consists of two cylindrical glass bulbs connected below by a bent glass tube; it thus resembles a large U-tube with the limbs enlarged into bulbs. One bulb of each pipette (except *h*) is packed with glass tubing or rolls of iron gauze. This bulb ends above in a capillary tube which is connected by a short piece of rubber tubing with one of the side-tubes of the main capillary. The other bulb of the pipette is open to the air.

In some forms of the Orsat apparatus, the pipette *h* and the palladium tube *f* are omitted. For convenience in description, the use of the simpler form of apparatus is explained first, and the description of this part of the apparatus is given later.

To prepare the apparatus for an analysis, lubricate each of the taps with vaseline; fill the measuring-tube with water;

and fill the pipettes with the appropriate reagents. The reagents used are the same as in the Hempel pipettes; fill the pipette *b* with potassium hydroxide, the pipette *c* with sodium hyposulphite, and the pipette *d* with ammoniacal cuprous chloride.

In order to be sure that the apparatus is gas-tight, close the

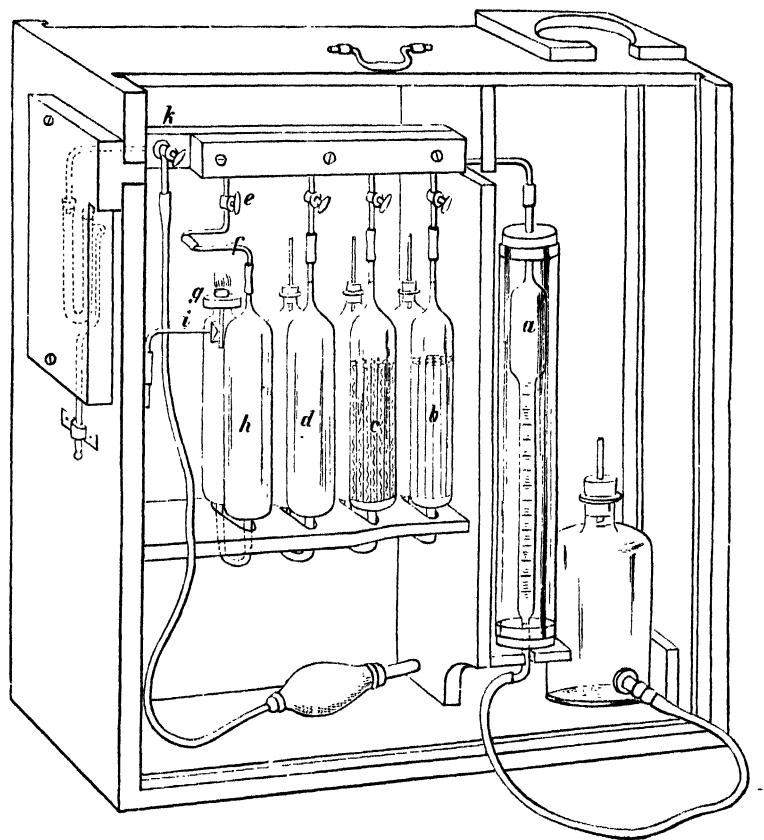



FIG. 80.—Lunge-Orsat Apparatus.

pipette taps and the tap *k*, and place the levelling-bottle on the top of the box. If the level of the water in the measuring-tube does not alter in the course of two minutes, the apparatus is ready for an analysis.

Open the tap *k*, and raise the levelling-bottle until the measuring-tube is filled with water. Then close the tap *k*, open the tap above the pipette *b*, and lower the levelling-bottle so

that the potassium hydroxide solution is drawn up until it completely fills the absorption bulb. *Do not allow the reagent to reach the tap*, but close the tap when the liquid reaches the mark upon the capillary tube between the bulb and the tap. Open the tap *k*, and expel the air again from the measuring-tube. In a similar manner, remove the air from the other absorption bulbs.

Collection of the Sample.—As the apparatus is portable, the sample is drawn directly into the measuring-tube. Close the pipette taps, after expelling the air from the absorption bulbs. Fill the measuring-tube with water. Connect one of the free openings of the tap *k*, with a tube leading to the flue (or other source of the gas), and connect the other opening with the small rubber pump. By means of the pump, draw the gas to be analysed through the leading tubes until it has completely displaced the air. (In order to prevent admission of dust into the apparatus, it is advisable to pass the incoming gas through a tube packed with cotton-wool.) Then turn the tap *k* so as to bring the inlet tube into communication with the measuring-tube. Lower the levelling-bottle, and allow a little more than 100 ml. of the gas to enter the measuring-tube.

Close the tap *k*, and remove the connections from it. Adjust the position of the levelling-bottle so that the surface of the water in it is level with the lowest graduation mark. Open the tap *k* for a few seconds, and then close the tap. In this way, 100 ml. of the gas, at the atmospheric pressure and at the temperature of the water jacket, is obtained.

Analysis of the Gas.—The plan of the operations is identical with that adopted in using the Hempel apparatus. The gas is treated with the various reagents in the order prescribed on p. 417. Carbon dioxide is first absorbed by means of potassium hydroxide in the pipette *b*, as follows:—Open the tap above the pipette *b*, and drive the gas into the pipette by raising the levelling-bottle. When the water reaches the top of the measuring-tube, close the rubber tube with a clip between the measuring-tube and the levelling-bottle. *The water from the measuring-tube must not be allowed to enter the capillary tube.*

On account of the large surface of reagent exposed to the gas, absorption is rapid; it is still more rapid if the gas is kept moving to and fro between the pipette and the measuring-

tube, as the reagent on the glass tubes in the pipettes is thereby constantly renewed. When returning the gas to the measuring-tube, *take care that the reagent does not reach the tap above the pipette*.

Allow exactly one minute for the water to drain from the sides of the measuring-tube, and read the volume of the gas. Repeat the above series of operations until the volume remains unaltered.

The absorption of oxygen by sodium hyposulphite in pipette *c*, and of carbon monoxide by the ammoniacal cuprous chloride in pipette *d*, is performed in a similar manner.

Notes.—The reagents used in the pipettes must be frequently renewed, as they are not protected from the atmosphere as in the Hempel double-pipette.

The determination of carbon dioxide, in this as in all other forms of apparatus in which water is used as the liquid in the burette, is inaccurate. It could be made as accurate as the determination of the other gases by using mercury in the burette, but the apparatus would no longer be portable.

At the completion of a set of analyses, empty the pipettes. If any reagent has got into the capillaries or taps, wash it out at once with water. Lubricate the taps before packing away the apparatus.

Determination of Hydrogen by Combustion in Contact with Palladium

If a mixture of hydrogen and excess of oxygen is passed over palladium black, complete combustion of the hydrogen takes place. The reaction is slow at the ordinary temperature, but at 100° it is almost instantaneously complete. Methane and its homologues are not burned under the same conditions, but combustion of the methane becomes appreciable when the temperature reaches 200°. These facts form the basis of the following method for the determination of hydrogen.

The capillary tube *f* (Fig. 80) contains a thread of asbestos coated with palladium black. The capillary tube and its contents can be heated by means of a small spirit-lamp *g*. The method of using the apparatus is as follows :—

Fill the bulb *h* with water, expelling the air as described on p. 426. Determine the carbon dioxide, oxygen, and carbon

monoxide. Then lower the levelling-bottle, open the tap *k*, allow air to enter until the total volume is nearly 100 ml., and close the tap *k*. Read the volume accurately. Gently heat the capillary *f* by means of a *small* flame, and pass the gas very slowly from the measuring-tube into the pipette *h*. If hydrogen is present in quantity, the first portion of the palladinised asbestos will glow on account of the heat liberated by the combustion. The glowing portion should not be more than 1 mm. in length.

Return the gas to the burette, and measure the volume. Any trace of carbon monoxide is also burned. (Usually a trace of the carbon monoxide escapes absorption by the cuprous chloride in this apparatus.) If any methane is present, a minute fraction of it will also be burned. Remove any carbon dioxide, therefore, by means of potassium hydroxide, and again measure the volume.

Two volumes of hydrogen require one volume of oxygen for combustion, so that two-thirds of the total contraction represents the volume of hydrogen. If any carbon dioxide is found after the combustion, a correction must be applied. The following example of an analysis shows the method of calculation :—

			Per cent.
Initial reading . . .	100 ml.	Carbon dioxide	. 8·8
After potassium hydroxide .	91·2 ml.		
		Oxygen . .	8·0
After sodium hyposulphite .	83·2 ml.		
		Carbon monoxide .	6·1
After cuprous chloride . .	77·1 ml.		
After addition of air . .	99·4 ml.		
After burning the mixture .	89·8 ml.	Hydrogen . .	6·0
After removing carbon dioxide	89·2 ml.		

It is not possible satisfactorily to correct for the carbon dioxide found after the combustion, if both carbon monoxide and methane are present in the mixture. The matter is not of any practical importance, as the Orsat method is not capable of yielding very accurate results ; a rough correction will make any error from this source smaller than other errors inherent in the method. When carbon monoxide is burned, the contraction is equal to half the volume of the carbon dioxide

produced, whereas, when methane is burned, the contraction is equal to twice the volume of the carbon dioxide produced. The assumption is therefore made that the gas yielding carbon dioxide was partly methane and partly carbon monoxide, and that the contraction on its combustion is equal to the volume of the carbon dioxide produced.

The total contraction on combustion (after removal of the carbon dioxide) was 10·2 ml. Of this, 0·6 ml. was carbon dioxide. The contraction due to the combustion of the hydrogen was therefore :

$$10{\cdot}2-(0{\cdot}6\times 2) = 9{\cdot}0 \text{ ml.}$$

Of this 9·0 ml., two-thirds was hydrogen and one-third oxygen ; the volume of hydrogen present was therefore 6·0 ml.

The Haldane Apparatus

For the analysis of air in mines, the Haldane apparatus is commonly employed. Mercury is used as the confining liquid, and thus any error due to solubility of carbon dioxide or other gases is eliminated. The burette consists of a wide top portion, joined to a graduated tube of narrow bore at the bottom which enables very small alterations in volume of the gas to be observed accurately. This is essential in determining the percentage of carbon dioxide in air by an absorption method. A slow-combustion pipette is included in the apparatus by means of which carbon monoxide, hydrogen, and methane can be determined.

Analyses Involving the Use of a Lunge Nitrometer

THE Lunge nitrometer (Fig. 81) consists of two glass tubes connected by a stout rubber tube. The levelling-tube L is ungraduated and is open to the air; the measuring-tube M is graduated and is fitted at the top with a three-way tap, so that the measuring-tube may be connected with either the cup C or the tube A. By means of this tap a sample of gas may be drawn into the apparatus through the tube A, and then, by turning the tap, any desired reagent may be run in from the cup C. The pressure tubing used to connect the two glass tubes should be a little longer than the measuring-tube, and must be securely wired on to the tubes.

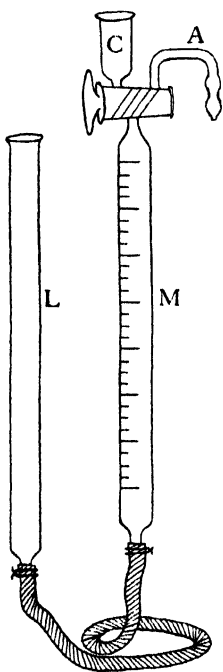



FIG. 81.

At all times the apparatus should stand on a mercury tray. Special clamps with wide grips may be obtained for holding the apparatus, but *good* burette clamps, with rubber pads on the grips, are quite satisfactory. Each tube, when filled with mercury, weighs about 3 lb., and the use of a flimsy burette clamp means the almost certain breakage of the apparatus.

Nitrogen in a Nitrate or Nitrite

OUTLINE OF METHOD.—The nitrate or nitrite is reduced to nitric oxide by shaking with mercury and concentrated sulphuric acid in the measuring-tube of a Lunge nitrometer. The nitric oxide is measured, and, from the volume of nitric oxide, the weight of nitrogen is calculated.

Procedure.—The solution containing the nitrate should not exceed 2 ml. in volume; if necessary, it must be evaporated until reduced to this volume.

Fill the measuring-tube of the nitrometer with mercury by raising the levelling-tube. Pour the nitrate solution into the cup C. By cautiously opening the tap, run the solution into the nitrometer without admission of any air. Wash out the vessel that contained the nitrate *with a few drops* of dilute sulphuric acid, and run this in through the cup in a similar manner. (Keep the volume of liquid and washings as small as possible—the total should not in any case exceed 4 ml.) Pour about 15 ml. of concentrated sulphuric acid into the cup and run this into the nitrometer, care being taken that no air is admitted. Remove the measuring-tube from the clamp and shake with a rotary motion, so that globules of mercury are thrown up into the liquid. In a minute or two the evolution of nitric oxide will begin. If no gas appears after shaking vigorously for two to three minutes, cautiously run in a few drops of water and shake again. The shaking must be continued until the evolution of nitric oxide ceases. Allow the apparatus to assume the room temperature, and then measure the volume of the gas under atmospheric pressure.

In order to adjust the pressure, assume the density of the aqueous liquid to be one-eighth that of mercury, and clamp the levelling-tube in the appropriate position. If the adjustment is correct, it will be found that a drop of liquid in the nitrometer cup is neither drawn in nor forced out when the tap is *very cautiously* opened. Care must be taken not to warm the gas by handling the measuring-tube.

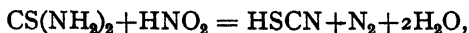
The temperature and the barometric pressure must be noted and the observed volume reduced to N.T.P. One ml. of nitric oxide at 0° and 760 mm. weighs 0·001340 gram, and corresponds to 0·000626 gram of nitrogen.

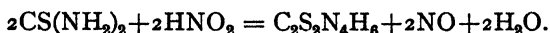
At the conclusion of an experiment, the measuring-tube may be readily cleaned by disconnecting and rinsing it three times with concentrated sulphuric acid, using 5 ml. each time.

Exercise.—Determine the percentage of nitrogen in potassium nitrate. Use about 0·2 gram.

Nitrite

When a nitrite is added to an acid solution of thiourea, the reaction that follows depends on the strength of the acid. In presence of a weak acid, such as acetic acid, the chemical change takes place almost entirely in accordance with the equation :

$$CS(NH_2)_2 + HNO_2 = HSCN + N_2 + 2H_2O,$$

whilst if hydrochloric acid is present, the interaction may be represented by the following equation :

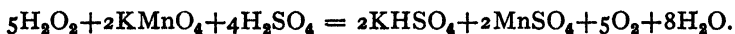
$$2CS(NH_2)_2 + 2HNO_2 = C_2S_2N_4H_6 + 2NO + 2H_2O.$$

In the first case, a little nitric oxide is always obtained, and in the second case a little nitrogen, but this does not affect the determination since the volume of gas obtained is the same in both cases. On account of the lower solubility of nitrogen, it is preferable to use acetic acid.

Procedure.—Weigh accurately about 0·15 gram of sodium nitrite. Introduce the weighed sample, together with about 0·2 gram of thiourea, into the cup of the nitrometer, and dissolve in 1 to 2 ml. of water. Run the solution into the measuring-tube and rinse the cup with *a few drops* of water. Then introduce 1 ml. of 50 per cent. acetic acid, and shake vigorously.

Gas is evolved immediately the solution is acidified, and the reaction is complete in a few minutes. In adjusting the levels, assume the density of the aqueous column to be one-thirteenth that of mercury. If the total volume of aqueous liquid is not greater than 4 ml., the error due to the solubility of the gas in water is negligible.

Hydrogen Peroxide

Hydrogen peroxide, in presence of sulphuric acid, interacts with potassium permanganate as follows :—

$$5H_2O_2 + 2KMnO_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 5O_2 + 8H_2O.$$

The concentration of a solution of hydrogen peroxide may therefore be determined by measuring the volume of oxygen obtained from a known volume of the peroxide solution on treatment with excess of permanganate.

The apparatus (Fig. 82) consists of a reaction vessel, together with a Lunge nitrometer. The reaction vessel consists

of a small conical flask with a well-fitting rubber cork which carries a glass tube. Connection with the tube A of a nitrometer is made by means of a piece of pressure tubing. A short wide test-tube is also required ; this must be slightly longer than the base of the flask in order that, when placed in the flask, it will remain in the position shown in the diagram.

Procedure.—Place 20 ml. of saturated potassium permanganate solution and 20 ml. of dilute sulphuric acid in the conical flask. Dilute 10 ml. of commercial hydrogen peroxide to 100 ml., and place 10 ml. of this diluted solution in the test-tube. Place the test-tube carefully in the flask, care being taken that no mixing of the peroxide and permanganate occurs at this stage. Insert the rubber cork and connect the flask with the nitrometer, which is filled with mercury. Loosen the tap of the nitrometer in its socket, and place the conical flask, up to the neck, in water at the room temperature. After about five minutes, adjust the mercury to the zero mark, insert the tap firmly into position, and turn it so that the reaction vessel is in communication with the measuring-tube. If the mercury level alters in the course of a few minutes, the temperature is not yet constant.

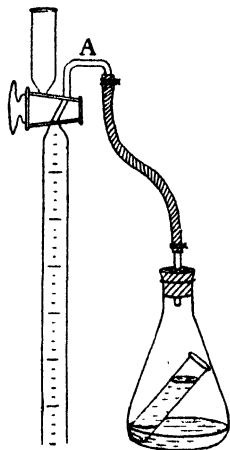



FIG. 82.

When the temperature has become constant, tilt the reaction flask so that the peroxide solution mixes with the permanganate. Keep the pressure approximately equal to the atmospheric pressure by lowering the levelling-tube from time to time. Rinse out the small tube with some of the permanganate solution by appropriate manipulation of the flask. When the reaction is apparently complete, shake the flask vigorously. (The liquid, unless violently agitated, may retain several millilitres of dissolved oxygen.)

Adjust the mercury levels and read the volume of oxygen. Reduce the volume to N.T.P. and calculate the weight of hydrogen peroxide per litre of the original solution.

The concentration of hydrogen peroxide is commonly expressed in terms of the volume of oxygen obtained from it

on decomposition by heat. Thus "ten volume" hydrogen peroxide solution yields ten times its own volume of oxygen at room temperature. (It may be pointed out that double this volume of oxygen is obtained when the peroxide is treated with permanganate.) Calculate the concentration of the peroxide solution in this way also.

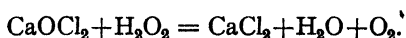
Valuation of Zinc Dust

Zinc dust is frequently used as a reducing agent, and an estimate of its value for this purpose may be obtained by measuring the volume of hydrogen evolved when a weighed sample is treated with excess of acid.

Place about 0·1 gram (accurately weighed) of the sample in the conical flask (Fig. 82) and add 25 ml. of water. In the small test-tube place 5 ml. of concentrated sulphuric acid. Proceed as described in the determination of hydrogen peroxide. From the volume of hydrogen evolved, calculate the percentage of zinc in the zinc dust.

Available Chlorine in Bleaching-Powder

Bleaching-powder and hydrogen peroxide interact as follows :—

$$CaOCl_2+H_2O_2 = CaCl_2+H_2O+O_2.$$

One ml. of oxygen at N.T.P. is equivalent to 0·00317 gram of available chlorine.

Measure into the conical flask (Fig. 82) 25 ml. of a solution of the bleaching-powder prepared as described on p. 151. In the small test-tube place 3 ml. of "ten volume" hydrogen peroxide. Proceed as described on p. 433. From the volume of oxygen evolved, calculate the percentage of available chlorine in the bleaching-powder.

Determination of Gases present only in Traces

METHODS depending on the alteration in volume produced by absorption are not suitable for the determination of traces of gases. An accuracy of 1 in 1000 in the measurement of a gas-volume is within the limits of what one would ordinarily regard as "permissible error." An illustration will make it clear that this error is far too large for many purposes. The amount of carbon dioxide in the atmosphere is usually about 3 parts in 10,000 or 0·03 per cent., and 0·03 ml. would be the alteration in volume produced by absorption of the carbon dioxide in 100 ml. of air. Even assuming that, by special precautions, the error of measurement were reduced to 1 in 10,000, there would still be an uncertainty of about 30 per cent. in the amount of carbon dioxide.

In practice, therefore, traces of gases are determined in a different manner. A large volume of the gas mixture is treated with a suitable absorbent, and the absorbed constituent is then determined by analysis of the reagent. For example, carbon dioxide in air may be determined by treating a large measured volume of air with a measured volume of standard baryta solution, and finding, by analysis, how much of the baryta has been converted into carbonate. The attainable accuracy is obviously greatly increased by the substitution of a chemical determination of the carbonate for the measurement of a minute alteration in a large volume. A comparatively rough measurement of the total volume is usually sufficiently accurate for a process of this kind.

Measurement of the Gas Mixture.—From the nature of the case, no general rules can be laid down. For the measurement of coal gas or other gas of which a large supply is available, a gas-meter is most convenient. The special description of the determination of carbon dioxide in air (see p. 438) may suggest a method that could be adapted to other cases.

Absorption Apparatus.—Convenient forms of apparatus for holding the absorption reagent are shown in Fig. 83, A,

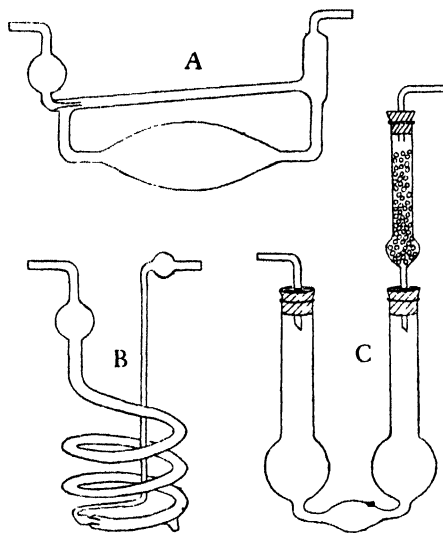



Fig. 83.

B, and C. If the gas contains dust, it must be passed through a tube packed with glass wool.

Sulphur in Coal Gas

Outline of Method.—The coal gas is burned in air and the sulphur dioxide formed is absorbed by a solution of sodium carbonate and bromine. All the sulphur is thereby obtained as sodium sulphate, and the sulphate is determined gravimetrically in the ordinary manner.

The gas is measured by a gas-meter and is led by the tube A into the glass flask B (Fig. 84). This is a 1-litre, round-bottomed, hard-glass flask with a short, wide mouth. The inlet tube must be of hard glass, and is drawn to a fine jet at C where the gas is burned. The air required for the combustion of the gas is freed from any traces of hydrogen sulphide in the laboratory atmosphere by passing it through the purifier E filled with pumice, upon which a concentrated solution of potassium hydroxide is constantly dropping from a tap funnel. The purified air then passes by the tube D into the flask B. The products of the combustion are drawn out of the flask by

means of a filter-pump through the tube F, and through three wash-bottles G, H, K, in which the sulphur dioxide is retained. The wash-bottles each contain sodium carbonate solution. To G and H a few drops of bromine are also added in order to oxidise the sulphite to sulphate.

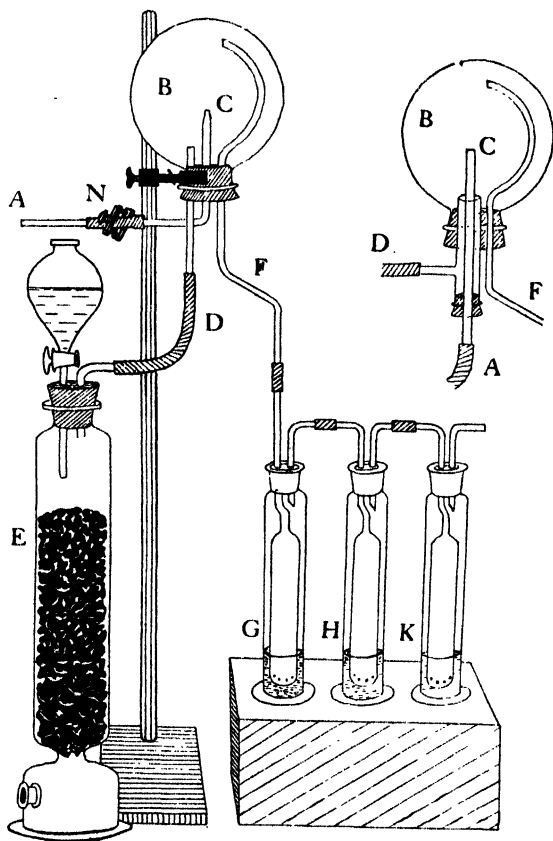



FIG. 84.

A larger, steady flame may be obtained by the modified arrangement of the gas and air supplies shown at the side of the diagram. The gas is led in through the central tube and the air through the outer tube.

Procedure.—Pass coal gas through the meter for a few minutes, burning the gas at a Bunsen temporarily connected

to C. Disconnect the Bunsen, and ignite the gas at C. By means of the screw-clip N, cut down the gas supply until the flame is about 10 mm. high ; then insert the cork in the flask. By regulation of the air and gas supplies, adjust the flame so that it burns with sharply defined edges.

When about 50 litres of gas have been burned, cut off the gas supply. Wash the contents of the wash-bottles G and H into a beaker, and rinse the flask B into the same beaker. Acidify the solution with hydrochloric acid, boil until the excess of bromine is expelled, and determine the sulphate gravimetrically as barium sulphate.

It is advisable to test the bromine used, because it sometimes contains sulphuric acid.

Atmospheric Carbon Dioxide

OUTLINE OF METHOD.—The sample of air, contained in a dry bottle of known capacity, is shaken with a measured volume of standard baryta solution which contains also barium chloride, until the absorption of the carbon dioxide is complete. The excess of barium hydroxide is determined by titration with standard hydrochloric acid, these operations being conducted in such a way that the baryta is protected from expired air. The process depends upon the insolubility of barium carbonate during the titration of the excess baryta with very dilute acid.

The following solutions are required :—

Fiftieth-normal Hydrochloric Acid.—Acid of approximately this concentration can be obtained by diluting 9·5 ml. of the concentrated acid to 250 ml., and again diluting 25 ml. of the latter to 500 ml. It is then standardised by means of borax, using methyl red as indicator, or by titration with standard baryta.

Fiftieth-normal Baryta.—Prepare this as described on p. 83, but only about 60 ml. of saturated baryta will be required for 1 litre of N/50 solution, and the barium chloride content should be about 40 grams per litre in order to reduce the solubility of barium carbonate.

The absorption bottle is a Winchester quart, the capacity of which has been previously determined. It is fitted with a rubber stopper with two holes, into one of which a glass tap is fitted, and a piece of glass rod is selected which will slide fairly tightly into the other.

Collecting the Sample.—By means of bellows or a suction-pump, fill the bottle with the air to be analysed, care being taken that expired air is not drawn into the bottle. Close the bottle with the rubber stopper, turning off the tap and closing the second hole with the glass rod. Note the temperature at the time of collection. (The error that may be introduced by assuming that the pressure is 760 mm. is less than other errors inherent in the method.)

Procedure.—Open the tap *in the open air* and immediately return the bottle to the laboratory, remove the glass rod and add about 2 ml. of phenolphthalein solution. Then at once run in 25 ml. of the baryta solution from the baryta burette through the hole from which the glass rod was removed. If a baryta burette outfit is not available the solution can be added from a pipette, but this must be operated by suction from the water pump or means adopted to avoid contact with expired air. A volume of 25 ml. of 0·02N baryta will be sufficient to absorb nearly five times the carbon dioxide content of outside air if the sample is taken in a Winchester quart, but more baryta should be used if the sample contains much more carbon dioxide than normal outside air. This would be indicated by the colour of the phenolphthalein disappearing altogether or becoming noticeably less. As soon as the baryta has been added, close the tap and replace the glass rod. Wet the whole of the inside of the bottle with the baryta solution, lay the bottle on its side, and shake it at frequent intervals during at least one hour. Then determine the excess of baryta by opening the tap, removing the glass rod and inserting the tip of the hydrochloric acid burette through the rubber stopper and titrating. The acid should be run in slowly, taking care to mix the contents of the bottle continuously to avoid a local excess of acid which might dissolve a little barium carbonate. Run the acid in until the pink colour of the phenolphthalein is almost discharged. Then remove the burette and allow the contents of the bottle to flow all over the inside, placing the glass rod in the open hole in the stopper to prevent entrance of carbon dioxide. It will be found that the baryta adhering to the sides of the bottle will cause the return of the pink colour. Add acid from the burette very slowly until this colour is just discharged after again wetting the sides of the bottle.

When the burette has been read a measured volume of

fresh baryta solution is titrated by the acid at once, in an atmosphere free from carbon dioxide. This can be done by adding, say, 10 ml. of the baryta solution to the bottle, *without* pouring out the liquid from the previous titration, and titrating with the acid. In this way any small error due to the action of a local excess of hydrochloric acid on barium carbonate near the end-point will be compensated for by a similar effect in titrating the additional barium hydroxide.

Example—

The volume of baryta solution added was 25 ml.

The volume of 0·0205N hydrochloric acid required for the excess of baryta was 19·54 ml., and the volume of acid required for an additional 25 ml. of baryta was 23·25 ml.

Hence (23·25—19·54) ml. of 0·0205N hydrochloric acid is equivalent to the carbon dioxide contained in the sample of air.

Now 1 ml. of N HCl is equivalent to 11·13 ml. of CO_2 at N.T.P.

Therefore 3·71 ml. of 0·0205N HCl is equivalent to $11{\cdot}13 \times 3{\cdot}71 \times 0{\cdot}0205 = 0{\cdot}847$ ml. of CO_2.

The volume of the Winchester quart was 2575 ml., so that the sample of air taken was (2575—25) ml. = 2550 ml., and the temperature was 15° C. The carbon dioxide in the sample of air was therefore—

$$\frac{0{\cdot}847 \times 10{,}550}{2550} = 3{\cdot}44 \text{ vols. in } 10{,}000 \text{ vols. of air.}$$

(10,550 volumes at 15° are equal to 10,000 volumes at 0° C.).

If the sample was collected at a temperature greatly exceeding the temperature of the laboratory, a correction may be made for the amount of carbon dioxide that enters the bottle with the outdoor atmospheric air (containing about 3 parts of carbon dioxide in 10,000) when the bottle is opened at the start of the analysis. For a temperature difference of 10°, the correction is approximately equivalent to a deduction of 0·1 volume of carbon dioxide in 10,000 volumes of air.

Note.—The sample of air should not be taken by emptying water out of the bottle in the atmosphere to be tested, since carbon dioxide may be given up by the water, especially when

the temporary hardness is high. The error may amount to more than 100 per cent.

Hydrogen Sulphide in Coal Gas

After measurement, the gas is dried by passing it over calcium chloride. The hydrogen sulphide is then absorbed by passing the gas through U-tubes containing pumice impregnated with copper sulphate and, at the exit end, a little calcium chloride. The pumice is prepared for use by soaking it in a hot, saturated copper sulphate solution and then drying it for four hours at 150° to 160°.

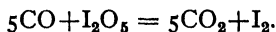
The increase in weight of the U-tubes gives the amount of hydrogen sulphide.

Sulphur Dioxide in Flue Gases

A measured volume of the gas is drawn through a tube containing cotton-wool to remove dust and then through a solution of sodium carbonate and bromine (see p. 437). The sulphate formed is determined gravimetrically.

Determination of Carbon Monoxide (in Traces)

For this purpose the gas is passed over heated iodine pentoxide, which reacts with the carbon monoxide according to the following equation :—

$$5CO+I_2O_5 = 5CO_2+I_2.$$

A measure of the amount of carbon monoxide present is obtained by titration of the iodine formed with very dilute thiosulphate. Unsaturated hydrocarbons, and reducing gases, such as hydrogen sulphide or sulphur dioxide, must first be removed from the gas. Contact with organic matter must be avoided, so that the tube containing the iodine pentoxide must be carefully cleaned, and no greased stoppers or corks used.

Procedure.—Fill a U-tube, without taps but with side tubes, with alternate layers of iodine pentoxide and broken glass, and seal the wide ends. Place this in a bath of oil which is to be maintained at 150°. Connect one side tube to an absorption tube such as that illustrated in Fig. 83 A, p. 436.

This is filled with 10 per cent. potassium iodide solution to such a level that the gas entering the left limb drives the liquid along the upper tube, and thus causes it to circulate while the iodine is being absorbed. The tubes must be touching in order to minimise the amount of rubber surface exposed. A train of wash-bottles is fitted up, the first containing fuming sulphuric acid, the second ordinary concentrated sulphuric acid, and the third concentrated potassium hydroxide solution. This last is connected to the entrance tube of the iodine pentoxide vessel. The purpose of these reagents is to absorb any unsaturated hydrocarbons, sulphur dioxide or hydrogen sulphide. Select an aspirator bottle (K, p. 289) equal in volume to that of the gas to be passed, and fill it with water. Connect this with the exit tube of the potassium iodide absorption tube, attaching a screw-clip to the rubber connection.

Draw a slow current of the gas through the whole apparatus until the aspirator bottle is empty, this being made possible by a long exit tube attached to the aspirator bottle, to give the necessary fall of water.

Disconnect the potassium iodide tube, wash out the contents into a beaker and titrate the iodine by means of N/1000 sodium thiosulphate. Calculate the percentage of carbon monoxide, assuming the volume of gas passed is that of the aspirator bottle.

PART VIII

WATER ANALYSIS

Pure and Natural Water.—Natural water is never ideally pure water. It always contains, in solution or suspension, inorganic and organic substances derived from the air, the soil, and the rocks with which it comes into contact; and it may have become polluted, directly or indirectly, with sewage or other waste products of life and industry.

The substances that may be present in a natural water are chiefly (1) calcium, magnesium, and sodium salts, in the form of bicarbonate, chloride, sulphate, and nitrate; (2) comparatively small amounts, or traces, of iron and ammonium salts, nitrite, and phosphate; (3) dissolved gases—carbon dioxide, oxygen, and nitrogen; (4) organic matter, in solution or suspension; (5) living organisms, including bacteria.

Purpose of Water Analysis.—An examination of a water supply is generally made for the purpose of deciding whether the water is suitable for domestic or industrial purposes. In the case of a water intended for drinking, it is necessary to ascertain that the salts present are not objectionable, either as regards their nature or their amount, and that the water does not contain more than a mere trace of organic matter.

For washing and scouring, it is desirable to use what is familiarly known as a "soft" water, *i.e.* a water containing comparatively small amounts of calcium and magnesium salts. For steam-raising purposes, a soft, alkaline water free from substances that produce hard scale, corrosion, or priming, has many advantages; and many important industries, such as brewing, paper-making, and dyeing, are dependent upon a satisfactory water supply. The water best adapted for domestic use is equally suitable for many technical purposes; but the presence of certain salts may be desirable for one manufacturing process and objectionable for another.

Methods of Examination

The investigation of a water supply includes an examination of (1) the source from which the water is derived; and (2) the water itself. The two main sources of water suitable for general purposes are:—

(*a*) Ground Water, *i.e.* wells and springs.
(*b*) Surface Water, *i.e.* streams and rivers.

The Examination of the Source of the supply is directed mainly to the detection of pollution or of possible sources of pollution. The importance of this examination lies in the fact that a water supply, although satisfactory as a rule, may be liable to *occasional* pollution which an analysis of the water itself may fail to disclose. A careful inspection of the source may, in fact, render a complete analysis of the water almost superfluous, and it will, in any case, assist in the correct interpretation of the analytical results.

Shallow wells are often liable to pollution, on account of either their position or their unsatisfactory construction. It may be possible to remove the source of pollution, or to prevent the impurity reaching the well. In the case of river water, pollution—either from sewage or other waste products draining into the river, or from cultivated land through which the river flows—is almost inevitable, and river water must always be purified by storage and efficient filtration before it can form a satisfactory water supply for household purposes.

The Examination of the Water comprises (1) a physical and chemical examination; (2) a microscopical examination; and (3) a bacteriological examination. In what follows, only the physical and chemical methods of examination will be considered, but if the water is to be used for drinking, a bacteriological examination is essential.

When a water supply is intended for a drinking water, it is usually desirable to make a comprehensive investigation, involving most of the qualitative and quantitative determinations described below. If the water is to be used for industrial purposes, a more restricted examination will generally suffice —the chief constituents of importance in that case being dissolved oxygen, and the bicarbonates, sulphates, and chlorides associated with calcium and magnesium.

The results of the quantitative determinations are usually expressed in parts per 100,000 of water which, it may be noted, correspond to milligrams per 100 ml.[1]

COLLECTION OF SAMPLES OF WATER

At least 2 litres of water are required for a fairly complete analysis. Samples are most conveniently collected in Winchesters. The bottles should be of light-coloured glass. Before being used for samples, the bottles must be carefully rinsed with water, and should be filled completely with the rinsing water at least once. Bottles intended for holding water samples should be reserved for that purpose alone. For convenience and safety during transport, the bottles may be placed upright in wicker baskets or in padded boxes made for the purpose.

If the sample is to be collected from a tap, the water should be allowed to run to waste for several minutes before filling the bottle. In taking a sample from a river, loch, cistern, etc., the closed bottle should be wholly immersed in the water, and the stopper then withdrawn. Before the bottle is filled, it should be rinsed out several times with the water. The bottle is then completely filled, a little water is poured away, and the clean stopper—which should also be rinsed with the water—is firmly inserted. It is sometimes advisable to secure the stopper in its place by tying over it a piece of clean linen cloth. The bottles containing the samples should be labelled with a distinctive number or letter, and a note made of the exact place where each sample was taken, with the hour and date of collection.

An analysis of a single sample affords information regarding the state of the water only at the time the sample was taken, and, as many waters vary in character from time to time, it is often necessary to make a periodic examination. After heavy rain, for example, some waters are often turbid; and pollution is frequently intermittent. An endeavour should be made to obtain samples, not only when the water is in its normal state, but also when its condition is abnormal.

The examination of the water should be commenced as soon as possible after the sample is collected.

[1] Results are sometimes given in grains per gallon; to convert them into parts per 100,000, divide by 0·7.

PHYSICAL EXAMINATION

The physical examination includes the colour, turbidity, odour, and taste of the water, and the determination of its electrical conductivity.

Odour.—When the bottle is first opened, ascertain whether the water has any odour. If it has little or none, warm 100 ml. to about 50° in a clean flask, shake briskly, and try again. Good water has no smell, even when warmed.

Turbidity.—Examine the water contained in a large flask or bottle of colourless glass, and note its general appearance, *i.e.* whether it is bright and perfectly clear, or whether it is opalescent or turbid. If the turbidity is very pronounced, it may be desirable to ascertain approximately the amount of suspended matter.

Filter a measured volume (100 ml. to 1000 ml. according to the degree of turbidity) through a tared Gooch crucible containing a *thick* pad of asbestos, or through a very fine sintered glass crucible. Dry the crucible and contents in the steam-oven, cool, and weigh. Express the results in parts per 100,000.

Taste.—It is inadvisable to taste water samples indiscriminately, and, in any case, taste and smell are often difficult to differentiate. The presence of iron, salt, peat, etc., may confer on water a characteristic taste, but the presence of these substances can be ascertained in other ways. Pure water, properly aerated, may be described as tasteless.

Colour.—Special apparatus is often used to measure the colour of water, but for most purposes it is sufficient to note the colour (and turbidity) of the water, contained in a 100 ml. Nessler tube, as compared with a similar column of distilled water.

Distilled water is practically colourless when examined in this way. The presence of organic matter may confer a pale yellow tint. Moorland water containing peaty substances is often decidedly yellow or even reddish-brown.

Conductivity.—The conductivity of ideally pure water, expressed in gemmhos,[1] is about 0·04 at 18°, whereas that of ordinary distilled water is from twenty-five to one hundred times greater, say about 3 gemmhos. Natural waters have a much greater conductivity than distilled water, on account of

[1] 1 gemmho = $1{\cdot}0 \times 10^{-6}$ "reciprocal ohm."

the saline substances dissolved in them. The conductivity of natural waters varies from about 30 for a soft water like that of Loch Katrine, to 1000 or more for very hard or alkaline waters common in England, and to about 50,000 for sea water. If a water contains but a small quantity of sodium salts, the conductivity is approximately proportional to the "hardness" of the water, and every 20 units of conductivity (at 20°) correspond, very roughly, to one "degree" of hardness (p. 461). For example, a sample of water was found to have a conductivity (at 20°) of 540, which indicates a hardness of from 25° to 30°. The hardness was found to be actually 27°.

A convenient, portable apparatus for conductivity measurements of this kind is the "Dionic Water Tester." The apparatus consists of a glass cell fitted with platinum electrodes, and a small continuous-current dynamo which is connected with the electrodes and with a direct-reading conductivity meter. The dynamo is turned by hand, and the conductivity of the water in the cell is registered on a dial provided. The only correction is for temperature, and the measurement occupies but a few moments.

The determination of conductivity is a most convenient and rapid method of *periodically* testing one and the same water supply. Any abnormal variation in the amount of dissolved salts—which can only be due to an influx of water of a different character and, it may be, from an objectionable source—is at once readily detected.

CHEMICAL EXAMINATION

The chemical examination includes the determination of, more especially, the dissolved solids, ammonia, dissolved oxygen, reducing power, chloride, nitrite, nitrate, "hardness," acidity or alkalinity, and the action of the water on metals—especially lead. For some purposes, an accurate analysis of the saline constituents may also be required.

Total Solids

(Residue on Evaporation)

The residue obtained by evaporating a sample of water to dryness consists of all the non-volatile inorganic and organic substances that were dissolved or suspended in the water. If

the water is very turbid, it is usually desirable to determine the solid matter in suspension, as described on p. 446. The filtered water is then used for the determination of the dissolved solids.

The quantity of water that should be evaporated depends on the probable amount of the saline constituents, and from 100 ml. to 500 ml. is usually sufficient. If the sample contains 10 parts of dissolved solids in 100,000, the residue from 250 ml. weighs 0·025 gram.

Procedure.—Place a clean platinum basin in an air-oven at 180° for several minutes, then cool in a desiccator for ten minutes, and weigh.

Measure the water in a graduated flask, transfer about 50 ml. to the basin and evaporate on the steam-bath. Add more of the water at intervals, and finally rinse the flask with a little distilled water and add this to the basin.

After complete evaporation, remove the basin, wipe the outside carefully, and place it in an air-oven at 180° for an hour. Cool in a desiccator for ten minutes, and weigh. The residue is often hygroscopic. Replace the basin, therefore, in the air-oven for fifteen minutes, and weigh again as rapidly as possible after cooling. Repeat until a constant weight is attained.

The results are not comparable unless the residue is always dried at the same temperature. Dried at 100°, the residual salts retain much combined water (water of crystallisation). Calcium sulphate retains half a molecule at 107°, and magnesium sulphate and calcium chloride 1 molecule even at 180°.

After weighing, heat the dish gently over a Bunsen flame, in order to obtain an idea of the amount of organic matter present in the residue. Observe whether the residue changes colour (becoming yellow, brown, or black). A smell of singed horn indicates the presence of *nitrogenous* organic matter. It may be noted, however, that if the residue contains much nitrate, very little charring will occur although organic matter is present.

The residue may be used to test for phosphate, as described on p. 460.

"Free" Ammonia and "Albumenoid" Ammonia

Ammonia is often present in natural water, in the form of ammonium salts, and is usually referred to as "free" or "saline" ammonia. By distilling the water with a little

sodium carbonate, the ammonia is found in the first portion of the distillate.

The so-called "albumenoid" ammonia is obtainable by distilling the water with alkaline potassium permanganate solution after the removal of the "free" ammonia. The organic matter present in the water is decomposed by this treatment, but, as only a portion of the total organic nitrogen is thereby converted into ammonia, the results afford only an approximate measure of the nitrogenous organic substances present in the water.

The ammonia obtained in the distillates is determined colorimetrically by means of Nessler's solution, whereby 1 part of ammonia in 100,000,000 (0·01 mgrm. per litre) can be detected. This reagent is a mixture of potassium mercuric iodide (K_2HgI_4) and sodium or potassium hydroxide, and it gives a brownish-yellow coloration with extremely dilute ammonia solutions. On account of the delicacy of the test, and of the small amounts of ammonia usually dealt with, the colorimetric determinations of ammonia must be carried out in a room that contains no ammonia or ammonium salts, and not in the general laboratory.

The following materials are required :—

(1) *Nessler Solution.*—Dissolve (*a*) 3·5 grams of potassium iodide in 15 ml. of water ; (*b*) 1·7 grams of mercuric chloride in 30 ml. of water ; and (*c*) 12 grams of sodium hydroxide in 30 ml. of water. Add (*b*) to (*a*) gradually, while shaking, until a slight red precipitate remains permanent ; then add (*c*) and dilute the mixture to 100 ml. Finally, add a little of the mercuric chloride solution until a slight permanent turbidity again forms. Set the mixture aside until clear, and then decant into a bottle fitted with a rubber stopper.

Transfer a portion of the solution to a small bottle for immediate use (Fig. 28, p. 69). The pipette for measuring the solution is graduated to deliver about 2 ml. In order that the slight sediment that is sometimes present may not be disturbed, the pipette should not reach to the bottom of the bottle.

(2) *Standard Ammonium Chloride Solution.*—Dissolve 0·785 gram of pure ammonium chloride in water and dilute the solution to 250 ml. As required, dilute 10 ml. of this solution to 1 litre. One ml. of the dilute solution corresponds to 0·01 mgrm. of ammonia.

(3) *Ammonia-free Water.*—Ordinary distilled water frequently contains a trace of ammonia. In order to ascertain if this is the case, mix 50 ml. of the water with 2 ml. of Nessler solution. If no yellow coloration develops within three minutes, the water is fit for use. As a rule, it is necessary to prepare ammonia-free water in the following way :—

Add about 1 gram of recently ignited sodium carbonate crystals to about 2 litres of distilled water contained in a large flask or copper boiler. Distil the water and test 50 ml. of the distillate from time to time with Nessler solution. As soon as it ceases to give a coloration, collect the water in a clean Winchester. (Stop the distillation when the volume of water in the flask is reduced to about 250 ml.) Keep the Winchester stoppered and away from sources of ammonia.

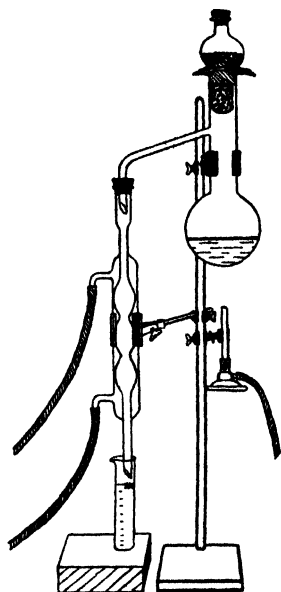



FIG. 85.

(4) *Alkaline Potassium Permanganate Solution.* — Dissolve 4 grams of potassium permanganate in 750 ml. of water, add 100 grams of sodium hydroxide, and boil the solution in a flask until the volume is reduced to about 500 ml. After the solution has become cold, transfer it to a stoppered bottle.

(5) *Ignited Sodium Carbonate.* —Heat some sodium carbonate crystals in a platinum crucible to dull redness for about half an hour, then allow to cool, and transfer to a stoppered bottle.

The Apparatus, Fig. 85, consists of a distilling flask of not less than 1 litre capacity, and a condenser. The distilling flask, if not fitted with a ground-in stopper, is closed with a tube on which a bulb is blown and which contains lead-shot in order to give it more weight; a piece of clean sheet rubber, in which a small hole is cut with a cork borer, is drawn over this tube below the bulb, and the bulb rests on and closes the mouth of the flask. The side-tube of the distilling flask should pass well down into the inner

tube of the condenser, and, if the tubes fit closely, no connecting cork need be used. If a rubber cork is used, it should be soaked in sodium hydroxide solution, and then thoroughly washed.

Preliminary Examination of the Water.—Measure 50 ml. of the sample into a Nessler tube, add 2 ml. of Nessler solution, and mix. From a burette, run 0·5 ml. of the standard ammonium chloride solution into another tube, fill to the mark with ammonia-free water, add 2 ml. of Nessler solution, and mix. If the colorations are of about equal intensity, use 500 ml. of the water for the determination. As a rule, half a litre of a drinking water is a suitable quantity. If less than half a litre is taken, dilute the measured quantity to 500 ml. with ammonia-free water.

"Free" Ammonia.—Rinse the flask and condenser with hydrochloric acid, and then wash thoroughly with water. Place about 200 ml. of distilled water and about 1 gram of recently ignited sodium carbonate in the flask, and distil[1] fairly rapidly with a free flame. Allow the steam to blow through the condenser for several minutes, then admit the condensing water, and collect the distillate in Nessler tubes. Continue the distillation until the distillate gives no coloration with Nessler solution.

When the apparatus has been proved in this way to be ammonia-free, remove the flame and introduce, through a long-stemmed funnel which has been previously steamed, 500 ml. of the water (or other suitable quantity, as determined by the preliminary examination), and proceed with the distillation. Distil fairly rapidly and as regularly as possible, and collect the distillate in three portions of 50 ml. each, using Nessler tubes as receivers. Then interrupt the distillation and allow the apparatus to remain for the determination of the "albumenoid" ammonia in the residue. The whole of the ammonia in the portion of water taken is now contained in the distillate, and is determined colorimetrically as described below.

Determine the ammonia in the *second* portion of the distillate before the first portion is examined, in case the first portion contains too much ammonia (more than 0·1 mgrm.) for accurate comparison. To the second portion add 2 ml. of Nessler solution and mix with the stirring-bulb. (The stirring-bulb

[1] In the case of a mineral water containing hydrogen sulphide, add 5 ml. of a 0·5N solution of lead acetate before the distillation.

must not be laid on the bench but should be kept in a beaker containing distilled water.) Then ascertain, by trial, how much of the standard ammonium chloride solution must be diluted to 50 ml. (with ammonia-free water) to give a coloration of equal intensity. The full intensity of the colour is not obtained immediately the reagent is added, and an interval of three minutes should elapse before the solutions are compared.

The Nessler solution must always be added to the solution containing ammonia, not *vice versa*. If the solution contains more than 0·1 mgrm. of ammonia in 50 ml., the coloration is too intense for accurate comparison. The coloration given by 2 to 3 ml. of the standard ammonium chloride solution is the most suitable.

If the second portion requires not more than 2 ml. of the standard ammonium chloride solution to give a colour of equal intensity, the *whole* of the first portion should be examined in the same way. If the second portion requires more than 2 ml., take one-half of the first portion (after mixing it well) and dilute to 50 ml. with ammonia-free water before adding the Nessler solution; the total ammonia in the first portion is then twice the observed quantity. Then test the third portion; it will probably contain very little or no ammonia.

From the total volume of the standard ammonium chloride solution required for the whole of the distillate, calculate the weight of ammonia in 100,000 parts of the water. One ml. of the standard solution corresponds to 0·01 mgrm. of NH_3, and if 4 ml. in all were required, and 500 ml. of water used, the water contained 0·008 part of "free" ammonia in 100,000.

"Albumenoid" Ammonia.—Add to the contents of the distillation flask 50 ml. (one-tenth of the volume of water used) of the alkaline permanganate solution, and continue the distillation until four portions of 50 ml. have been collected. Test each portion of the distillate, beginning with the last one.

Calculate the amount of "albumenoid" ammonia that 100,000 parts of the water would yield.

Dissolved Oxygen (Winkler's Method)

Dissolved oxygen is an important factor in the corrosion of boilers, etc., and its determination is necessary in controlling boiler feed water.

Prepare the following solutions :—

Dissolve 40 grams of manganese chloride ($MnCl_2, 4H_2O$) in water and dilute to 100 ml.

Dissolve 50 grams of sodium hydroxide and 15 grams of potassium iodide in 50 ml. of hot water, cool and dilute to 100 ml.

The determination depends on the action of the dissolved oxygen on manganese hydroxide, resulting in the formation of higher hydrated oxides, which are then dissolved in hydrochloric acid in presence of potassium iodide. Iodine equivalent to the dissolved oxygen is liberated, and this is then titrated with standard thiosulphate. The interaction of the manganese hydroxide with the dissolved oxygen must be carried out with exclusion of atmospheric oxygen. This may be effected by filling a stoppered bottle completely with the water sample, and adding the necessary reagents at the bottom of the bottle by means of long pipettes. It is, however, rather difficult to mix the contents of a completely filled bottle, and the following method avoids this difficulty.

Fit a 500 ml. graduated flask with a cork, bored with a small hole and one slightly larger. Through the smaller hole insert a thin wall glass tube, long enough to reach to the graduation mark on the flask, for introduction of an inert gas. The other hole must be large enough to allow a small pipette to be inserted loosely. Fill the flask with the water sample up to the graduation mark, and using a graduated pipette, draw out 7 ml. of water from the flask and discard this volume. There will now be room for addition of the various reagents even though the graduation mark is high up on the neck of the flask. Now replace the cork and pass a current of hydrogen, nitrogen, or coal-gas to displace the air, and while the gas is still passing slowly, add 1 ml. of concentrated sulphuric acid (from a graduated pipette) and 2 mls. of 0·1N potassium permanganate to oxidise any nitrite present. It is not necessary to deliver these or further reagents to the bottom of the flask, since oxygen is not present in the space over the liquid. Fit a short piece of glass rod tightly into the open hole in the cork, and by means of a screw clip, close the rubber tube supplying the gas, as near as possible to the glass tube in the cork. Mix the contents of the flask thoroughly, and allow to stand for ten minutes. In event of the colour of the permanganate disappearing, add 1 ml. more of the reagent and allow a further

ten minutes to ensure complete oxidation. When this has been effected, the slight excess of permanganate must be destroyed by adding 1 ml. of 0·1N sodium oxalate solution. During all additions of reagents a current of the inert gas must be passed into the flask.

An alternative method for destroying nitrite has recently been used by Cohen and Ruchhoft (*Ind. Eng. Chem. Anal.*, Edn., 1941, 622). In this modification 4 ml. of a solution made by dissolving 1·0 gram of sulphamic acid in 50 ml. of water, and adding 50 ml. of *cold* 10 per cent. sulphuric acid, is used in place of the sulphuric acid, potassium permanganate and sodium oxalate described above. This amount of sulphamic acid is sufficient to destroy the nitrite in a 500 ml. sample if the nitrite nitrogen is as high as one part in 100,000 of water. After mixing the water with the sulphamic acid solution ten minutes is allowed for the elimination of nitrite.

After the nitrite has been destroyed by either of these methods, add 2 ml. of the manganese chloride reagent and 5 ml. of the sodium hydroxide-potassium iodide reagent. Mix thoroughly, taking the same precautions to avoid access of air, as described under the addition of sulphuric acid and potassium permanganate. Allow the flask to stand for about ten minutes out of bright daylight. Then add 6 ml. of concentrated hydrochloric acid and again mix thoroughly. The dark coloured precipitate previously formed will dissolve, and iodine equivalent to the oxygen absorbed from the water will be liberated. As air will not appreciably affect the solution after acidification, the contents of the flask are poured into a 750 ml. beaker, the flask rinsed and the iodine titrated with 0·05N sodium thiosulphate. No appreciable error will be introduced if the volume of the water is taken as 500 ml., since, although 7 ml. of water was removed before adding the reagents, the dissolved oxygen contained in the latter will be approximately the same as that in 7 ml. of an average sample of water. (The total volume of the reagents will actually be greater than 7 ml., but some of them contain much less dissolved oxygen than water).

If V_1 = the volume of 0·05N thiosulphate used in the titration of the 500 ml. water sample, the volume of oxygen at N.T.P. in a litre of the water $= \frac{V_1 \times 0{\cdot}05}{1000} \times 5595 \times 2$ ml., since 8 grams of oxygen occupy 5595 mls. at N.T.P.

Reducing Power

(Organic Matter)

The organic matter in natural waters is mainly of plant or animal origin, and consists essentially of the decomposition products of decayed vegetation and of substances derived from the animal organism. Many of these organic substances—more particularly those derived from animal sources—contain nitrogen, and one of the simplest methods of obtaining information regarding the amount of organic matter in natural waters is the determination of the "albumenoid" ammonia, already described.

The organic matter is more or less easily oxidised, and an approximate estimate of the organic impurities in a water may also be arrived at by determining its reducing power, or its power of "absorbing" oxygen. The reducing power of a water is usually ascertained by measuring its action on a dilute acid solution of potassium permanganate. The following solutions are required :—

(1) *Potassium Permanganate Solution* (N/80).—Dissolve 0·395 gram of the pure salt in cold water, and dilute the solution to 1 litre. (One ml. corresponds to 0·1 mgrm. of available oxygen.)

(2) *Dilute Sulphuric Acid.*—Pour 100 ml. of pure concentrated sulphuric acid into 300 ml. of water, cool the mixture partially, and add dilute potassium permanganate solution, drop by drop, until the acid acquires a permanent pink tinge.

(3) *Sodium Thiosulphate Solution* (N/250).—Dissolve 1 gram of the pure salt in 1 litre of water.

(4) *Potassium Iodide Solution.*—Dissolve 10 grams in 100 ml. of water.

Procedure.—Measure 250 ml. of the water to be examined into a perfectly clean, stoppered bottle (500 ml.). Place the bottle in a thermostat or air-bath at 27°, and, when the temperature of the water has become constant, add 10 ml. of the dilute sulphuric acid and 10 ml. of the potassium permanganate solution. Allow the bottle to remain in the bath for four hours. Examine it from time to time, and if a marked

diminution in the depth of the pink colour is observed, add another 10 ml. of the permanganate solution.

Meanwhile standardise the sodium thiosulphate solution as follows:—Place 250 ml. of freshly distilled water in a 500 ml. bottle, add 10 ml. of the sulphuric acid, 10 ml. of the permanganate solution, and then 1 ml. of the potassium iodide solution. Titrate the liberated iodine with the thiosulphate, starch solution being used as indicator as usual. The volume of thiosulphate solution required corresponds to 1 mgrm. of available oxygen.

After the lapse of four hours, remove the bottle containing the water sample and cool the contents by immersing the bottle in water. Add 1 ml. of the potassium iodide solution, and titrate with the thiosulphate.

If 30 ml. of the thiosulphate correspond to 1 mgrm. of oxygen, and if 24 ml. were required after digesting the water with the permanganate, the amount of oxygen absorbed by 250 ml. of the water is $\frac{30-24}{30} = 0{\cdot}2$ mgrm., *i.e.* 0·08 part per 100,000.

Chloride

All natural water contains chloride. Rain water may contain only a mere trace, and river water less than 1 part of "chlorine" in 100,000, but a much larger quantity is often present, especially in well water.

The following solutions are required:—(1) A solution of silver nitrate containing 4·79 grams per litre. One ml. of this solution corresponds to 1 mgrm. of chlorine. (2) A 2 per cent. solution of potassium chromate, free from chloride (see footnote on p. 171).

Procedure.—Measure 100 ml. of the water into a porcelain basin, add 1 ml. of the potassium chromate solution, and run in the silver nitrate solution from a burette while stirring briskly, until a faint permanent reddish-brown tinge is obtained. Usually, too much silver nitrate is added in the first titration. Add, therefore, a few drops of ammonium chloride in order to destroy the reddish tinge, and use this mixture, which has a pure yellow colour, as a guide for a second titration made in another similar basin. On account of the solubility of silver chromate, a slight excess—about 0·2 ml.—of silver nitrate

must be added before the reddish tinge (precipitated silver chromate) is apparent. The number of millilitres of silver nitrate solution used, less 0·2 ml., gives the milligrams of chloride ion (Cl) in 100 ml. of the water, *i.e.* parts per 100,000.

Alternative Procedure.—To 100 ml. of the water, add 1 ml. of the potassium chromate solution. Run in the silver nitrate solution until, after stirring, a permanent reddish tinge is obtained. Then add, from a measuring-cylinder, more of the water sample until the reddish tinge is just destroyed. (From 5 to 20 ml. may be required.) The volume of silver nitrate solution used corresponds to the chloride in 100 ml. of the water plus *one-half* of the further quantity of water added. Calculate the number of millilitres of silver nitrate solution required for 100 ml. of the water.

Notes.—If the water contains less than 1 part of chloride ion in 100,000, use a larger volume and evaporate on the steam-bath to about 100 ml., then cool, and titrate.

If the water is acid, add sodium bicarbonate (sufficient to render the water faintly alkaline) before titrating. A "blank" determination of chloride should be carried out on the same weight of sodium bicarbonate as that added.

If the water is peaty and highly coloured, or if it is sewage-polluted and contains hydrogen sulphide, add a small quantity of lime-water prepared from Iceland spar to the measured portion of the water; pass a current of carbon dioxide through the liquid, then boil for a few minutes, cool, and filter. Determine the chloride in the filtrate as directed.

Nitrite

Nitrite is rarely found in natural waters, except in minute traces, and a qualitative test is usually all that is necessary. The following solutions are required :—

(1) *Griess-Llosvay Reagent.*—Dissolve (*a*) 0·1 gram of *a*-naphthylamine by warming with about 40 ml. of water mixed with 10 ml. of glacial acetic acid, (*b*) 0·5 gram of sulphanilic acid in the same quantities of hot water and acetic acid. Mix the solutions (*a*) and (*b*), and dilute to 300 ml. If the solution becomes coloured by keeping, shake with a little zinc dust, and filter.

(2) *Standard Potassium Nitrite Solution.*—Dissolve 0·268 gram of pure barium nitrite [$Ba(NO_2)_2, H_2O$] in hot water, add excess of potassium sulphate (about 0·25 gram) in solution, cool, and dilute to 1 litre. (Keep this solution in the dark.) For immediate use, dilute 5 ml. of the clear liquid to 1 litre. This solution contains 0·05 part of nitrite (NO_2) in 100,000.

Detection of Nitrite.—To 50 ml. of the water sample, add 2 ml. of the reagent, and warm to about 80°. If nitrite is present, a pink coloration is obtained. With as little as 0·01 part of nitrite (NO_2) in 100,000, the colour appears almost immediately, and much smaller amounts give a decided reaction within a few minutes.

Quantitative Determination.—Place 50 ml. of the water sample and of the standard nitrite solution in two Nessler tubes, and add 2 ml. of the reagent to each. Cover the tubes (in order to protect the contents from any trace of nitrite in the air), and set them aside for twenty minutes. If, on then comparing the tubes, the water sample is found to give a darker coloration than the standard, use a smaller quantity of the sample and dilute with water (free from nitrite) to 50 ml.; if the water sample contains less nitrite than the standard, dilute the latter; and, in either case, repeat the experiment until the tints in the two Nessler tubes match one another.

The amount of nitrite (NO_2) in the water can then be calculated.

Nitrate

Practically all natural waters contain at least a trace of nitrate. Nitrate, like chloride, is itself innocuous, but, from a hygienic standpoint, the presence of a large amount of nitrate in a drinking water is by no means unimportant.

Detection of Nitrate.—In a test-tube, mix 1 ml. of the water, drop by drop, with 3 ml. of concentrated sulphuric acid, cool, and then add a few milligrams of brucine.

If nitrate is present, a red coloration is obtained. With 10 parts of nitrate (NO_3) in 100,000, the colour is cherry-red changing to orange; with 1 part, it is rose-red; and with 0·1 part, a pale rose-coloured solution is obtained.

In case the sulphuric acid contains a trace of nitrate, it is essential to make a parallel experiment with distilled water,

and, if nitrate is present, to compare the coloration with that given by the water sample. Nitrite gives no coloration with brucine and sulphuric acid, provided the above directions are followed exactly. Ferrous salts interfere, and, if present, must therefore be removed by means of sodium hydroxide free from nitrate.

Quantitative Determination.—The nitrate is reduced to an ammonium salt by means of a copper-zinc couple, and the ammonia is then determined by means of Nessler solution. From 10 ml. to 100 ml. of the water, according to the amount of nitrate present, is required for the determination. If about 1 part of nitrate (NO_3) in 100,000 is probably present, use 50 ml.

Preparation of the Copper-Zinc Couple.—Roll a piece of zinc foil, 7·5 cm. square, into a cylinder about 2 cm. diameter. Dip the foil into hydrochloric acid in order to clean it, and then wash it with water. Place it in a large test-tube, and cover it with a 3 per cent. solution of copper sulphate for a few minutes until it is completely coated with a black deposit of copper. Pour away the copper sulphate solution, and wash the foil with distilled water without removing it from the test-tube.

Reduction of the Nitrate.—If the water contains much ammonia, dilute the measured portion as necessary to about 100 ml., and boil it until the volume is reduced to about 50 ml. Cool the water, transfer it to the test-tube containing the copper-zinc couple, and add dilute hydrochloric acid (3 to 4 drops) sufficient to cause, after several minutes, a slight evolution of hydrogen. Cover the test-tube with a watch-glass, and set aside overnight.

The reduction is more rapid at higher temperatures, and at 50° it is complete in an hour.

Determination of the Ammonia.—Place about 400 ml. of distilled water and about 1 gram of ignited sodium carbonate in an apparatus similar to that used for the determination of ammonia in water, and remove any ammonia in the apparatus by distilling over about 100 ml. Transfer the solution containing the reduced nitrate to the distilling flask, add the washings of the copper-zinc couple, and distil. Collect the distillate in two portions of 50 ml., and determine the ammonia in each portion colorimetrically, as described on p. 451.

From the amount of ammonia thus found, calculate the

corresponding amount of nitrate (NO_3). Any nitrite in the water is of course included, but the amount is usually too small to affect the result appreciably.

Alternative Method.—This method posseses the advantage over the previous one that any nitrite present does not affect the determination of the nitrate. The process consists in matching the yellow colour produced by the interaction of the nitrate in the water with phenol sulphonic acid, and subsequent treatment with ammonia, against that produced by a known amount of nitrate.

The following solutions are required :—

(1) *Standard Nitrate Solutions.*—Dissolve 0·072 gram of potassium nitrate in 1 litre of water. One ml. corresponds to 0·01 mgrm. of nitrogen as nitrate.

(2) *Phenol Sulphonic Acid Reagent.*—Weigh into a small conical flask 4 grams of phenol, add 2 ml. of water, and 25 ml. of concentrated sulphuric acid. Heat the flask on the water-bath for two to three hours.

Procedure.—Measure 10 ml. of the water sample, and 10 ml. of the standard nitrate solution, into two small dishes. Evaporate both liquids to dryness, and to each add 1 ml. of the reagent. Moisten the residues by rotating the dishes carefully, and then heat each dish on the water-bath for at least five minutes. Cool, dilute with distilled water, and transfer the contents of each dish to a Nessler tube. Add to each 1 : 1 ammonia until a yellow colour develops or the solution is alkaline. Make up each solution to the 100 ml. mark with distilled water, and compare the depths of colour. Into a measuring-cylinder, pour off so much of the darker solution that the depths of colour remaining are the same. From the volume of the darker solution required, calculate the nitrate content of the water, and express the results as parts of nitrogen per 100,000.

Phosphate

Phosphate is rarely present in natural waters, except in traces. As a rule, only a qualitative test need be made.

Dissolve the residue obtained in the determination of the "Total Solids" (p. 448) in dilute nitric acid; transfer the solution to a procelain basin, and evaporate to dryness on the steam-bath. Moisten the residue with nitric acid, and again

evaporate to complete dryness. Then add a few drops of nitric acid and 5 ml. of water, warm, and filter. Add 5 ml. of ammonium molybdate solution, warm to about 60°, and set aside. If phosphate is present, a yellow turbidity, or a distinct precipitate, is obtained, and its amount may be approximately estimated by comparing it with known amounts of ammonium phospho-molybdate.

Hardness

Natural waters are familiarly described as "hard" or "soft," these terms having reference to the action of the water on soap. A water is said to be "soft" if it gives an immediate lather with soap, and "hard" if a lather is obtained with difficulty. The "hardness" of a water thus refers to its soap-destroying power; part of the hardness disappears on boiling, and is called "temporary," that which remains being called "permanent."

Hardness is due almost entirely to the presence of calcium and magnesium ions. In most natural waters a portion of these ions correspond to the bicarbonate ion content of the water, and the remainder to other acidic ions. Boiling decomposes the bicarbonate ion, and thus causes precipitation of the greater part of the carbonate ions thereby formed as calcium and magnesium carbonates, some 2 parts per 100,000 of calcium carbonate, and 10 parts per 100,000 of magnesium carbonate remaining in solution. The diminution in hardness produced by boiling is the temporary hardness, while the magnesium and calcium ions remaining owing to the solubility of their carbonates, together with those corresponding to the other acidic ions, are the cause of permanent hardness.

Whatever the constituents may be, both temporary and permanent hardness are expressed as their equivalent of calcium carbonate in parts per 100,000 of the water. In this country, 1° of hardness corresponds to 1 part of calcium carbonate in 100,000 of water.

The hardness of a water, or its soap-destroying power, may be determined by means of a standardised solution of soap. The soap solution is gradually added to a measured volume of the water until, after vigorous agitation, a permanent lather is obtained. The hardness determined in this way corresponds *approximately* to the amount of calcium and

magnesium salts dissolved in the water. When it is necessary to ascertain the respective amounts of these salts accurately, the calcium and magnesium must be determined gravimetrically as described on p. 470, but for many practical purposes sufficient information is obtained more expeditiously by the volumetric methods described below.

Temporary Hardness or "Alkalinity."—The bicarbonates of calcium and magnesium are, as a rule, the only substances in a natural water which, on account of hydrolysis, confer alkalinity (as shown by certain indicators) on the water, and the bicarbonate hardness is sometimes referred to as the "alkalinity" of the water. The "alkalinity" is determined as follows:—

Measure 100 ml. of the water into a casserole. Add 2 ml. of methyl red, and run in 0·02N hydrochloric acid until the liquid becomes light red. Boil for about a minute to expel carbon dioxide; if too much acid has not been added, the yellow colour of the indicator will reappear. Add more acid, drop by drop, until the first sign of a red tinge, which is not destroyed by further boiling, is obtained. A more convenient and expeditious method of procedure is to add excess of acid (about 1 ml. in excess) and then, after boiling for about a minute, to titrate back with 0·02N baryta solution. The end-point of the titration is sharply defined.

One ml. of 0·02N acid corresponds to 0·001 gram of $CaCO_3$; and, since 100 ml. of the water was taken, each millilitre of the standard acid used in the titration represents 1 part of calcium carbonate in 100,000 parts of water, or 1° of hardness.

This method of determining temporary hardness includes any calcium or magnesium carbonates that the water may contain in solution. It also makes no allowance for the calcium and magnesium carbonates which would remain in solution if the water were boiled, and so gives a somewhat higher value than the true temporary hardness as defined above.

Some natural waters contain sodium carbonate, and in that case a correction, referred to below, must be applied to the "alkalinity" before it is taken as a measure of the bicarbonate hardness.

Permanent Hardness.—Measure 250 ml. of the water into a conical flask, preferably of Pyrex glass, and boil for fifteen minutes. Make up 250 ml. of a decinormal alkali solution by

mixing about 100 ml. of decinormal sodium hydroxide with 150 ml. of decinormal sodium carbonate. Add 25 ml. of this mixture to the solution in the flask, and boil the liquid down to not more than half its original volume. By this process magnesium is almost completely precipitated as well as calcium. Cool, and make up to 250 ml. by rinsing into a standard flask with distilled water. Filter through a dry filter, rejecting the first 20 ml. or so, and titrate 50 ml. of the solution with 0·02N hydrochloric acid, using methyl red as indicator, and boiling off carbon dioxide as described above under "Temporary Hardness."

Take a further 25 ml. of the alkali solution, dilute it to 250 ml., and titrate 50 ml. of this with the 0·02N hydrochloric acid in the same manner.

From the difference between the two titrations, calculate the permanent hardness in parts of calcium carbonate per 100,000 parts of water.

If the original water contains sodium carbonate, there can be no permanent hardness, and, in the foregoing determination, the filtrate will require *more* acid than that necessary to neutralise the alkali added to the water. The excess represents the amount of sodium carbonate originally present in the water, and it must be deducted from the "alkalinity" in order to find the bicarbonate hardness.

Total Hardness by means of Potassium Palmitate.—In this method a measured volume of the water is made acid to methyl orange and the carbon dioxide removed by boiling. After cooling, alkali is added until the liquid is just acid to phenolphthalein, and it is then titrated with a standard solution of potassium palmitate.

The solution of potassium palmitate is prepared by mixing together 100 ml. of 90 per cent. alcohol, or methylated spirits, and 62 grams of glycerine, and adding 6·41 grams of pure palmitic acid. Warm the mixture on the water-bath, shaking occasionally, until the solid has dissolved. Partially cool the solution, add 2 ml. of phenolphthalein, and run in an alcoholic solution of potassium hydroxide containing about 2 grams in 50 ml. of alcohol until the solution turns faintly pink. Make up to 250 ml. with 90 per cent. alcohol or with methylated spirits, adding a little more potassium hydroxide solution during dilution if necessary to maintain the very faint pink

colour, which must be finally discharged by the cautious addition of N/10 hydrochloric acid.

This solution of potassium palmitate must be standardised by titration against a standard solution of barium chloride containing 3·053 grams of pure $BaCl_2, 2H_2O$ in 500 ml. of solution. If 10 ml. of this solution and 190 ml. of distilled water are used, the volume of potassium palmitate solution required will be about 5 ml., a volume similar to that which would be used in determining the hardness of water of average quality, taking a sample of 200 ml.

The standardisation of the palmitate solution and the determination of the hardness of the sample of water are carried out as follows. Measure out 10 ml. of the barium chloride solution and about 190 ml. of distilled water, or 200 ml. of the water to be analysed, into a conical flask. Add 1 ml. of methyl orange, and run in decinormal hydrochloric acid drop by drop until the solution is just pink; then add 5 drops in excess. Boil for two minutes to expel carbon dioxide, cool, transfer to a white dish, and add 1 ml. of phenolphthalein. Run in decinormal sodium hydroxide drop by drop until a pink colour is visible, and then just discharge this with the least possible amount of decinormal hydrochloric acid. Titrate with the solution of potassium palmitate, using preferably a burette of 10 ml. capacity, until a faint pink colour is visible, indicating that all the barium or calcium and magnesium has been precipitated as insoluble palmitate, and a slight excess of reagent is present, causing the change in colour of the phenolphthalein through its hydrolysis. It is advisable to make sure that the end-point has been reached by adding a further 0·1 ml. of the palmitate solution, and observing that the pink colour persists for one minute.

If a ml. are required for the titration of the barium chloride solution, and b ml. for 200 ml. of water, the total hardness of the water is $12{\cdot}5 \frac{b}{a}$ degrees.

In cases in which the total hardness is less than 1°, or when the magnesium content is relatively high, special precautions are necessary to obtain satisfactory results. These are described by W. H. Kitto (*Analyst*, 1938, 63, 168).

Calcium and Magnesium.—The water is evaporated with ammonium carbonate. The dry residue, containing the

calcium and magnesium as carbonates, is extracted with hot ammonium carbonate solution which dissolves the magnesium carbonate, but is practically without action on the calcium carbonate. The amount of the latter is ascertained, and gives the hardness due to calcium salts. The difference between the total hardness and that due to calcium salts gives the hardness due to magnesium salts.

Measure 100 ml. of the water into a platinum basin, add 10 ml. of a 2 per cent. solution of ammonium carbonate (2 grams of the solid and 1 ml. of concentrated ammonia in 100 ml.), and evaporate to dryness on the steam-bath. Pour 15 ml. of the same ammonium carbonate solution into the basin, bring the liquid into contact with the whole of the residue, and allow the basin to remain on the steam-bath for about two minutes. Filter through a 5½-cm. paper, retaining the undissolved carbonate as far as possible in the basin. Repeat the extraction twice, using about 10 ml. of ammonium carbonate each time.

Rinse the platinum basin four times with 90 per cent. alcohol, and wash the filter with the same alcohol until the filtrate is free from alkali. (Absence of alkali may be ascertained by allowing about 5 ml. of the filtrate to drop into a little water containing methyl red and a trace of 0·02N acid.) Dissolve the calcium carbonate, which now alone remains in the basin and on the filter, in 10 ml. of 0·1N hydrochloric acid, and titrate the excess of acid with 0·02N baryta solution, using methyl red as indicator.

The amount of calcium in the water, expressed in degrees of hardness, is then calculated. If the hardness due to calcium is found to be 6° and the total hardness was 10°, the hardness due to magnesium corresponds to 4°. Degrees of hardness are expressed in terms of calcium carbonate, but it is a simple matter to convert the results into milligrams of calcium and magnesium per litre, or any other more convenient units.

Alternative Method.—In this method, which may be found preferable for very hard waters, the calcium is precipitated as oxalate and is determined by titration with standard potassium permanganate solution.

Measure 100 ml. of the water into a glass basin, add 1 ml. of dilute hydrochloric acid, and heat until almost boiling. To the hot solution, add ammonia until it is alkaline and then 3 ml. of a freshly prepared saturated solution of ammonium

oxalate. Evaporate on the steam-bath until the volume of the liquid is about 10 ml. Add 10 ml. of ammonia, filter the calcium oxalate through a small paper, and wash with warm water containing a little ammonia until the filtrate is free from chloride. Pierce the apex of the filter paper with a pointed glass rod, and wash the precipitate into a small conical flask. Heat 5 ml. of dilute sulphuric acid in the original glass basin (in case any of the precipitate remains in it), and pour the hot acid into the filter, care being taken that the acid comes into contact with every part of the paper. Rinse the basin and wash the filter with hot water. Titrate the hot solution with 0·02N potassium permanganate.

The permanganate solution should be standardised by means of a dilute solution of calcium chloride of known concentration (prepared from calcite) under conditions similar to those described above.

Hydrion Concentration

Ideally pure water is neutral, but natural waters may be neutral, acid, or alkaline, according to the substances dissolved in them.

The so-called "alkalinity" of a water, as determined by titration (compare temporary hardness), is really a measure of the *potential* alkalinity of the water, and not of its *actual* alkalinity. The potential alkalinity of a solution of sodium bicarbonate, for example, as determined by titration with methyl orange as indicator, is the same as that of a solution of sodium hydroxide of the same molecular concentration; whereas sodium bicarbonate solution appears neutral, and sodium hydroxide solution alkaline, when tested with phenolphthalein. The actual alkalinities of these solutions are, in fact, very different, and it is on the actual acidity (or alkalinity) that many of the properties of a solution, such as the rate of its action on metals, depend.

As stated on p. 63, it is now customary to refer only to the hydrion concentration, or, better still, to the *p*H of a solution, instead of using the terms "acidity" or "alkalinity." Drinking waters which contain bicarbonates have a *p*H value between 7 and 9, while those from igneous rocks have a lower value.

The determination of *p*H in the case of a sample of water requires special precautions, as its value is easily affected by

small amounts of impurities, such as alkali from any glass with which it comes in contact. A change in the carbon dioxide content will also alter the value of the *p*H. Further, the addition of unsuitable indicators, though of the correct *p*H range, may cause a change in the true *p*H of a sample, as water is practically unbuffered (see p. 270, footnote). For these reasons an accurate determination of the *p*H of a sample of water can only be carried out by means of an electrometric method using a glass electrode (p. 196), taking special precautions to preserve the carbon dioxide equilibrium unchanged. In many cases, however, results of sufficient accuracy for the purpose may be obtained either by the electrometric methods described on pp. 193-196 or by the colorimetric method employing indicators (p. 269).

Notes.—Hard water—if the hardness is due mainly to bicarbonate—is alkaline, and soft water is often acid. If the acidity of a soft water containing bicarbonate is due entirely to carbonic acid, the water will become alkaline on passing a current of air, free from carbon dioxide, through the water. The acidity must be due to some acid other than carbonic acid if this treatment does not remove it. It should be noted, however, that a water from which the carbon dioxide has been entirely removed is no longer in equilibrium with normal air, and re-absorption of carbon dioxide commences *immediately* the water is exposed to ordinary air.

Lead

From a hygienic standpoint, it is most important that a water supply should not dissolve more than a mere trace of lead from the service pipes. Hard water, if the hardness is due to bicarbonate, is alkaline, and, as a rule, its only action is to coat the lead pipe with an insoluble film which adheres to the pipe, and practically no lead is found in the water. Soft water and moorland peaty water, which are often acid, not only tarnish lead but usually dissolve it, and the contamination may be such that the water is directly injurious to health. On the other hand, some very soft waters, such as the Glasgow water supply, are without appreciable solvent action on lead.

If a water supply is suspected of causing lead poisoning, samples should be taken after the water has been in contact

with the service pipes for various lengths of time, up to twelve hours.

Detection of Lead.—To 100 ml. of the water, add 2 ml. of acetic acid and 2 ml. of hydrogen sulphide solution. A brown coloration is obtained if the water contains more than 0·01 part of lead in 100,000. Iron does not interfere with the test, but copper gives a similar coloration. Copper is rarely present, however, in drinking water.

A very much smaller quantity of lead can be detected in the following way :—

Filter about a litre of the water through a small plug of pure cotton-wool placed in a funnel. Practically all the lead salt is retained by the cotton-wool. Redissolve the lead by pouring hot, dilute acetic acid over the cotton-wool, and then wash with distilled water. In this way the concentration of the lead may be increased almost a hundredfold. Test the solution with hydrogen sulphide.

Quantitative Determination.—If the hydrogen sulphide test shows the presence of lead, determine the amount colorimetrically as described on p. 262.

Action of Water on Lead

The action of a water on lead may be determined as follows :—

Procure some new ½-inch lead service piping, and cut it into lengths of 2½ feet. Close one end of each piece in a vice. The capacity of the tubes so formed is about 100 ml.

Carefully rinse out two or three of the tubes with the water under examination, and then fill the tubes *completely* with the water. Fill other two or three tubes with tap water that is known to be satisfactory as regards its action on lead. Cork the tubes so that no air is enclosed, and set them aside for twenty-four hours. Then empty the contents of the tubes into 100 ml. Nessler tubes, and determine the lead colorimetrically. Repeat the experiment until practically constant results are obtained.

When tested in this way, most waters will dissolve at least a trace of lead. The actual amount of lead found in the water taken from the tubes will probably be much more than would be present in a domestic water supply under ordinary circum-

stances, but with a really satisfactory water it should not be more than about 0·1 part lead in 100,000. A comparison with the amount of lead dissolved in the tubes containing the tap water is a useful guide.

Iron

Natural waters containing more than about 0·02 part of iron per 100,000 usually become opalescent or turbid on exposure to the air, owing to the decomposition and oxidation of the ferrous hydrogen carbonate. The precipitation of the iron as ferric hydroxide does not occur so readily in the case of a water containing peaty organic matter.

Quantitative Determination.—To 100 ml. of the water, add 5 ml. of concentrated hydrochloric acid and a few crystals of potassium chlorate, and evaporate to dryness. Dissolve the residue in 1 ml. of concentrated hydrochloric acid, dilute to 100 ml., and determine the iron colorimetrically by means of ammonium thiocyanate (p. 257) or thioglycollic acid (p. 258).

DETERMINATION OF THE SALINE CONSTITUENTS

An accurate analysis of the salts dissolved in a natural water is sometimes required, either for scientific or technical purposes. The analysis involves the determination of silica, iron, aluminium, manganese (rarely), calcium, magnesium, sodium, and potassium; and carbonate, sulphate, chloride, and nitrate.

Determination of Silica, Iron, Aluminium, Calcium, and Magnesium

Measure 1 or 2 litres of the water by means of a standard flask, add 10 ml. of concentrated hydrochloric acid, mix, and boil down to about 100 ml. in a silica vessel, adding more of the acidified water as the evaporation proceeds. Transfer the residual solution and the rinsings of the vessel to a platinum basin, and evaporate to complete dryness on the steam-bath.

Determination of Silica.—Add 2 ml. of concentrated hydrochloric acid to the dry residue and, after a few minutes, dilute with 10 ml. of water. Warm the covered basin on the steam-bath for several minutes, then filter through a small

paper, and wash the insoluble residue with warm water containing a little hydrochloric acid. Incinerate the paper and ignite the insoluble residue in a platinum crucible, and weigh. The "silica" must be examined for impurities as described on p. 343. It may contain calcium sulphate.

Determination of Iron, Aluminium, Calcium, and Magnesium.—To the filtrate from the silica, contained in a porcelain (not platinum) basin, add a few drops of concentrated nitric acid, evaporate to dryness, and ignite gently in order to destroy organic matter. Moisten the residue with 2 ml. of concentrated nitric acid, add 10 ml. of hot water, filter, and wash with warm water containing a little nitric acid. Determine the iron, aluminium, calcium, and magnesium as described on pp. 381-384.

Determination of Sodium and Potassium

Evaporate a measured volume of the water, in the manner already described, to about 100 ml. Transfer to a platinum basin and concentrate to 50 ml. To the hot solution, add a slight excess of a hot, saturated solution of barium hydroxide, in order to precipitate iron, magnesium, sulphate, etc. Evaporate until the volume of the liquid is about 25 ml., then filter the precipitate and wash it with hot water. The filtrate contains barium, calcium, sodium, and potassium. Remove the calcium and barium, and determine the sodium and potassium as described on p. 338.

Determination of Sulphate, Carbonate, Chloride, and Nitrate

Sulphate.—Determine whether much sulphate or only a small amount is present by adding one drop of dilute hydrochloric acid and a few drops of barium chloride solution to 10 ml. of the water; 10 parts, or more, of sulphate (SO_4) in 100,000 give an immediate precipitate.

Method 1.—Take 200 ml. of the water (or more if the precipitate with barium chloride is small and forms slowly), add about 2 ml. of dilute hydrochloric acid, and evaporate to about 50 ml., avoiding contamination with sulphur from coal-gas. Determine the sulphate as barium sulphate by the method described on p. 235, without adding water.

Method 2.—The determination of sulphate may be more rapidly carried out if a standard solution of potassium palmitate is available. The preparation of this solution is described on p. 463 under "Determination of Total Hardness."

Measure out 100 ml. of the sample into a conical flask. Add 1 ml. of methyl orange, and run in decinormal hydrochloric acid until the indicator is turned pink. Add five more drops of the hydrochloric acid, boil for two minutes to expel carbon dioxide, and to the hot solution add 10 ml. of 0·05N barium chloride. Boil again for two minutes, cool, and add 1 ml. of phenolphthalein. Run in decinormal sodium hydroxide drop by drop until a pink colour is visible, and then just discharge this with the least possible amount of decinormal hydrochloric acid. Now titrate with the standard palmitate solution until a pink colour is visible, as in the determination of total hardness on p. 463. After cooling, the solution may be transferred to a white dish if preferred for the subsequent treatment.

The palmitate solution must have been standardised against the above barium chloride solution, and the total hardness of the water determined by means of the same palmitate solution. Then, if x = the volume of potassium palmitate required by 10 ml. of 0·05N barium chloride solution diluted to 100 ml., y = the volume equivalent to the total hardness in 100 ml. of water, and z = the volume required for the titration of 100 ml. of the water as described above, then the volume of potassium palmitate equivalent to the sulphate in 100 ml. $= x+y-z$. Since the normality of the potassium palmitate solution is $\frac{0{\cdot}5}{x}$, 100,000 ml. of the water contains $\frac{48\times 0{\cdot}5(x+y-z)}{x}$ grams of SO_4.

Carbonate.—The total "alkalinity" of the water, as determined by titration with hydrochloric acid and described under "Hardness," gives the amount of carbonate (with bicarbonate) present.

One ml. of 0·02N acid corresponds to 0·6 mgrm. CO_3, and if 100 ml. of the water is titrated, each millilitre of the acid required corresponds to 0·6 part of carbonate in 100,000.

Chloride and Nitrate.—The determination of chloride and of nitrate has already been described.

SIGNIFICANCE OF THE RESULTS OF ANALYSIS IN THE CASE OF A DRINKING WATER

The purity of a drinking water is judged mainly from the amounts of nitrogenous substances (free and albumenoid ammonia, nitrite, and nitrate), organic matter (absorption of oxygen), and chloride that it contains. It is practically impossible to fix definite standards of purity based on the amounts of any of the above substances. A water must be judged on its own merits, and with full knowledge of the source from which it is derived, and especially on the result of a bacteriological examination. No attempt is here made to discuss the full significance of the results of analysis. A few notes are given below, and further information will be found in Thresh's *Examination of Waters and Water Supplies*.

Residue on Evaporation.—It is desirable that this should not exceed 50 parts per 100,000.

Hardness.—If the total hardness is under 5°, the water may be considered "soft"; from 5° to 10°, "fairly soft"; from 10° to 20°, "hard"; and over 20°, "very hard." If the hardness exceeds 30°, the water is very unsuitable for general purposes.

Chloride.—Sewage contains chloride, and the presence of much chloride in a water (especially if accompanied by an excessive amount of nitrate) may be an index of pollution—provided the chloride is not derived from sea water or other natural source. As a general rule, a surface water contains less than 2 parts of chloride ion in 100,000. Well water may contain much more.

Free and Albumenoid Ammonia.—Decaying organic matter and sewage contain ammonia, and the presence of more than about 0·005 part of free ammonia in 100,000 is significant of possible pollution. If a water yields more free ammonia than albumenoid ammonia, the nitrogenous impurity is probably derived from sewage. On the other hand, *slight* sewage pollution—sufficient to render a water unsafe—cannot always be detected by chemical methods. Peaty water yields the albumenoid ammonia slowly, and usually in larger amount than the free ammonia.

A satisfactory water seldom yields as much as 0·01 part of albumenoid ammonia per 100,000.

Dissolved Oxygen.—One litre of pure water at 15° C. will dissolve about 6·5 ml. of oxygen from air at ordinary pressures. The determination of dissolved oxygen is important not only in boiler feed water, when the question of corrosion is under consideration, but also in ascertaining the amount of dissolved oxygen taken up by effluents resulting from sewage disposal plants.

Reducing Power.—The absorption of less than 0·1 part of oxygen per 100,000 in the case of an upland surface water, and of less than 0·05 in the case of other waters, is usually regarded as indicating waters of satisfactory purity as regards organic matter. The result of any one determination is, however, rarely sufficient to condemn a water or to justify its use, and the amount of oxygen absorbed should be considered together with the yield of albumenoid ammonia.

Nitrite.—Nitrite may arise from the reduction of nitrate, but it occurs in sewage and manure, and it should be entirely absent from a drinking water.

Nitrate.—Nitrate, like chloride, is innocuous; but, as it is derived from nitrogenous organic matter of animal origin and is the final product of its decomposition, its presence in a water is an index of past pollution. It is not possible to fix a standard of purity in respect of nitrate, but a satisfactory surface water, even from cultivated land, seldom contains more than 1 part of nitrate ion in 100,000. Well water often contains a larger amount.

Acidity.—If the *p*H of a water is less than 6·5, the solvent action of the water on lead requires careful investigation.

Lead.—Drinking water should be entirely free from lead. On account of the cumulative nature of the poison, it is difficult to fix a limit to the amount of lead that is permissible in a water supply. If the amount never exceeds 0·03 part per 100,000, the water may probably be regarded as safe. A water supply which, under normal circumstances, is liable to contain up to 0·1 part of lead per 100,000 must be described as dangerous.

APPENDIX

LIST OF COMMON REAGENTS

Unless the contrary is stated, it is to be understood that any reagent mentioned in the text has the composition and concentration indicated below. For convenience, the quantity necessary for the preparation of a Winchester of solution is given in each case. A Winchester contains about 2500 ml.

For quantitative work it is usually necessary to prepare solutions as required, since the bench solutions, even when prepared from the purest chemicals, usually contain appreciable amounts of impurities dissolved from the glass.

Acids and Alkalis

The dilute acids and alkalis are 2N, with the exception of barium hydroxide and calcium hydroxide.

Concentrated Sulphuric Acid (Density 1·84) is approximately 36N. It often contains traces of lead, iron, and nitric acid.

4N Sulphuric Acid is prepared by diluting 270 ml. of the concentrated acid to a Winchester.

Dilute Sulphuric Acid (approximately 2N) is prepared by diluting 135 ml. of the concentrated acid to a Winchester.

Concentrated Nitric Acid (Density 1·42).—This is the constant boiling-point acid and contains about 68 per cent. of nitric acid. It is about 16N. The commonest impurities are chloride and sulphate.

Dilute Nitric Acid (approximately 2N) is prepared by diluting 300 ml. of the concentrated acid to a Winchester.

Concentrated Hydrochloric Acid (Density 1·17) is about 10·8N. It may contain traces of iron, arsenic, and sulphate.

Dilute Hydrochloric Acid (approximately 2N) is prepared by diluting 500 ml. of the concentrated acid to a Winchester.

Acetic Acid (approximately 2N) is prepared by diluting 280 ml. of glacial acetic acid (about 17N) to a Winchester.

Sodium Hydroxide (approximately 2N) is prepared by dissolving 200 grams of sodium hydroxide (" white sticks ") in a Winchester. It always contains carbonate and chloride, and may also contain sulphate, alumina, and silica.

Concentrated Ammonia (Density 0·880) is about 18N. The commonest impurities are carbonate, silicate, and aluminate (derived from glass bottles), and tarry matter.

Dilute Ammonia (approximately 2N) is prepared by diluting 250 ml. of concentrated ammonia to a Winchester.

Ammonium Carbonate (approximately 2N) is prepared by dissolving 200 grams of commercial ammonium carbonate (sesqui-carbonate), together with 100 ml. of 0·880 ammonia, in a Winchester.

Sodium Carbonate (approximately 2N) is prepared by dissolving 250 grams of the anhydrous salt, or 680 grams of the decahydrate (Na_2CO_3, 10 H_2O) in a Winchester. It usually contains traces of chloride and sulphate, and some samples are worthless on account of the amount of these impurities. It occasionally contains traces of ammonia.

Calcium Hydroxide (approximately 0·04N) is a saturated solution prepared from pure lime.

Barium Hydroxide (approximately 0·4N) is a saturated solution of barium hydroxide in water.

Other Common Reagents

Alcohol.—Rectified spirit contains 93 to 95 per cent. of ethyl alcohol. The " 66 over-proof " spirit contains 93 per cent. of alcohol.

Ammonium Chloride (approximately 2N) contains 260 grams of the salt, NH_4Cl, in a Winchester.

Ammonium Molybdate (approximately 3 per cent.) contains 75 grams of the salt, $(NH_4)_6Mo_7O_{24}$, $4H_2O$, in a Winchester.

Ammonium Oxalate (approximately 0·5N) contains 85 grams of the salt, $(COONH_4)_2$, H_2O, in a Winchester.

Ammonium Phosphate (approximately 0·5N) contains 55 grams of the salt, $(NH_4)_2HPO_4$, in a Winchester.

Ammonium Sulphide (approximately 2N) is prepared by saturating 1200 ml. of 2N ammonia with hydrogen sulphide, and then adding an equal volume of 2N ammonia.

Barium Chloride (approximately 0·5N) contains 145 grams of the salt, $BaCl_2$, $2H_2O$, in a Winchester.

Barium Nitrate (approximately 0·5N) contains 150 grams of the salt, $Ba(NO_3)_2$, in a Winchester.

Bromine Water (approximately 0·5N) is a saturated solution. It usually contains chlorine and iodine as impurities.

Calcium Nitrate (approximately 0·5N) contains 150 grams of the salt, $Ca(NO_3)_2$, $4H_2O$, in a Winchester.

Calcium Sulphate (approximately 0·03N) is a saturated solution.

Copper Nitrate (approximately 0·2N) contains 70 grams of the salt, $Cu(NO_3)_2$, $6H_2O$, in a Winchester.

Ferrous Sulphate (approximately N) is prepared by dissolving 335 grams of the salt, $FeSO_4$, $7H_2O$, together with 300 ml. of dilute sulphuric acid, in a Winchester.

Ferric Chloride (approximately 0·2N) is prepared by dissolving 45 grams of the salt, $FeCl_3$, $6H_2O$, in 50 ml. of concentrated hydrochloric acid and diluting to a Winchester.

Hydrochloroplatinic Acid.—This is usually obtained as the hydrate H_2PtCl_6, $6H_2O$, which contains 37·66 per cent. of platinum. In order to prepare a solution containing 10 per cent. of platinum (10 grams of platinum per 100 ml. of solution), dissolve 26·5 grams of this hydrate in about 50 ml. of water, filter, and wash the vessel and the filter two or three times with water. Dilute the filtrate and washings to 100 ml. The specific gravity of a solution containing 10 per cent. of platinum is 1·155 at 25°.

The preparation of this "10 per cent." solution from commercial platinum is described in Treadwell's *Analytical Chemistry*, vol. i. The recovery of platinum from residues by reduction with formic acid is described by M. Swisher (*J. Ind. Eng. Chem. Anal.*, 1939, 162).

Lead Acetate (approximately 0·5N) is prepared by dissolving 220 grams of the salt, $Pb(C_2H_3O_2)_2$, $3H_2O$, together with 30 ml. of glacial acetic acid, in a Winchester.

Mercuric Chloride (approximately 0·2N) contains 65 grams of the salt, $HgCl_2$, in a Winchester.

Mercurous Nitrate is prepared by dissolving 125 grams of the salt in 200 ml. of dilute nitric acid and 1250 ml. of water, and diluting to a Winchester.

Potassium Ferrocyanide (approximately 0·2N) contains 50 grams of the salt, $K_4Fe(CN)_6$, $3H_2O$, in a Winchester.

Potassium Chromate (approximately 0·2N) contains 50 grams of the salt, K_2CrO_4, in a Winchester.

Potassium Iodide (approximately 0·1N) contains 40 grams of the salt, KI, in a Winchester.

Sodium Acetate (approximately N) contains 325 grams of the salt, $NaC_2H_3O_2$, $3H_2O$, in a Winchester.

Stannous Chloride (approximately 0·2N) is made by dissolving 60 grams of the salt, $SnCl_2$, $2H_2O$, in 250 ml. of concentrated hydrochloric acid and diluting to a Winchester. A piece of tin placed in each bottle preserves the salt in the stannous state.

Silver Nitrate (approximately 0·1N) contains 40 grams of the salt, $AgNO_3$, in a Winchester.

PREPARATION OF PURE GASES

Carbon Dioxide.—This gas is prepared in a Kipp generator from marble and 4N hydrochloric acid. It must be washed and dried by passing it through a solution of sodium bicarbonate containing some solid, and then through concentrated sulphuric acid.

Hydrogen.—Hydrogen is prepared in a small Kipp generator from 6N sulphuric acid and arsenic-free zinc. A little copper sulphate solution should be poured over the zinc before this is placed in the Kipp. The gas must be purified and dried by passing it through a solution of mercuric chloride, then through an alkaline solution of potassium permanganate, and finally through concentrated sulphuric acid. Before the hydrogen is

used, it must be proved free from any appreciable amount of air by collecting a sample in a test-tube over water, and noting whether it burns quietly when ignited. If the gas must be oxygen-free, it must be passed over heated platinised asbestos before finally drying with sulphuric acid.

Oxygen.—Oxygen is prepared by heating potassium permanganate in a hard glass test-tube or small flask.

Any of these gases may be obtained in an almost pure condition from cylinders obtainable commercially.

Indicator Solutions

(See also p. 69.)

Bromo-phenol Blue.—Dissolve 0·5 gram in 1 litre of 20 per cent. alcohol.

Bromo-thymol Blue.—Dissolve 0·1 gram in water, add 1·6 ml. of 0·1N sodium hydroxide and dilute to 1 litre with water.

Cresol Red.—Dissolve 0·5 gram in 1 litre of 20 per cent. alcohol.

Litmus.—Dissolve 1 gram of azolitmin in 1 litre of water.

Methyl Orange.—Dissolve 0·05 gram of the solid in 1 litre of water.

Methyl Red.—Dissolve 0·05 gram of the solid in 800 ml. of alcohol, and dilute to 1 litre with water.

Methyl Yellow.—Dissolve 0·1 gram in 800 ml. of alcohol, and dilute to 1 litre with water.

Phenolphthalein.—Dissolve 1 gram of the solid in 500 ml. of alcohol, and dilute to 1 litre with water.

SOLUTIONS FOR ANALYSIS

It is customary for beginners to perform their first quantitative exercises with pure salts of known composition. There are many objections to this system—the most serious is that the exercise does not imitate the conditions met with in ordinary practice. For example, when working with a known quantity of material, the problem of how much precipitant to add does not, as a rule, present any difficulty; in this important particular, therefore, the exercise lacks much of the educational value it should possess. For this reason alone, it is desirable that all quantitative exercises should be performed with solids or solutions of " unknown " composition.

The most convenient system whereby a number of students can be provided with different exercises is to use standard solutions, and the following list may be found serviceable. All the solutions mentioned below can be prepared by weight from substances that are obtainable commercially in a pure state. The quantities given are the amounts required for the preparation of 1 litre of solution. With these concentrations, 20 to 30 ml. is a suitable quantity for an analysis. For small classes, the portions for analysis may be measured with a pipette or burette; for larger classes, it

is an advantage to store the solution in a bottle with a burette permanently attached, as shown in Fig. 29, on p. 83.

Aluminium	70 grams of ammonia alum, $(NH_4)_2SO_4$, $Al_2SO_4)_3$, $24H_2O$.
Ammonia	40 grams of dry ammonium chloride, NH_4Cl.
Arsenic	6 grams of arsenious oxide, As_2O_3, dissolved in dilute hydrochloric acid.
Barium	20 grams of barium chloride, $BaCl_2$, $2H_2O$.
Bromide	15 grams of dry potassium bromide, KBr.
Calcium	20 grams of pure calcspar, $CaCO_3$, dissolved in dilute hydrochloric acid.
Carbonate	100 grams of uneffloresced crystals of sodium carbonate, Na_2CO_3, $10H_2O$.
Chloride	20 grams of barium chloride, $BaCl_2$, $2H_2O$.
Chromate	20 grams of potassium dichromate, $K_2Cr_2O_7$.
Copper	30 grams of copper sulphate, $CuSO_4$, $5H_2O$.
Iodide	20 grams of dry potassium iodide, KI.
Iron	50 grams of ferric alum, $(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $24H_2O$.
Lead	20 grams of dry lead nitrate $Pb(NO_3)_2$. It is advisable to recrystallise this salt from a dilute nitric acid solution.
Magnesium	25 grams of magnesium sulphate, $MgSO_4$, $7H_2O$.
Manganese	Dissolve 20 grams of pure potassium permanganate in water, and pass sulphur dioxide until it is completely decolorised and the precipitated manganese dioxide has dissolved. Boil until free from sulphur dioxide, and dilute to 1 litre.
Mercury	10 grams of red mercuric oxide, HgO, dissolved in concentrated nitric acid, boiled, and diluted to 1 litre.
Nickel	70 grams of nickel ammonium sulphate, $NiSO_4$, $(NH_4)_2SO_4$, $6H_2O$.
Nitrate	16 grams (for reduction method) or 2·5 grams (for oxidation method) of dry potassium nitrate, KNO_3.
Phosphate	1·23 gram of microcosmic salt, $Na(NH_4)HPO_4$, $4H_2O$ (for the molybdate method).
Potassium	15 grams of dry potassium chloride, KCl.
Silver	20 grams of dry silver nitrate, $AgNO_3$.
Sulphate	25 grams of magnesium sulphate, $MgSO_4$, $7H_2O$.
Zinc	30 grams of zinc sulphate, $ZnSO_4$, $7H_2O$.

TYPICAL ANALYSES

Various Glasses

	SiO_2.	PbO.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O.	K_2O.	Total.
Table glass	70·61	0·70	...	...	4·92	11·95	12·28	100·46
Table glass	70·04	...	1·81		1·27	13·11	13·98	100·21
Plate glass	71·72	...	1·29	0·13	15·54	11·49	...	100·17
Mirror glass	77·35	...	...	...	1·25	15·05	6·33	99·98
White bottle glass *	68·64	...	2·83	0·71	14·94	13·01	...	100·37
Flint glass	42·65	43·17	0·28		0·28	...	13·89	100·27

* Contained also 0·24 per cent. of MnO. (Traces of Mn are almost invariably present in colourless glasses.)

Various Silicates

	SiO_2.	MgO.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
Albite	68·80	...	19·43	...	0·20	nil	11·68	...	100·11
Albite	67·99	...	19·23	...	1·84	1·25	9·69	...	100·00
Albite	68·40	...	19·89	...	...	0·90	10·69	...	99·88
Orthoclase	66·56	...	19·18	...	0·52	6·94	6·56	...	99·76
Orthoclase	66·58	...	21·26	...	1·18	0·76	10·26	0·16	100·20
A clay	63·69	...	17·02	10·18	0·97	...	4·02	4·05	99·93
Talc	63·42	31·49	...	0·57	...	...	...	4·38	99·86
Talc	62·78	31·16	...	1·85	...	...	...	4·32	100·11

Iron Pyrites

S.	Cu.	Fe.	Mn.	Zn.	Insoluble residue.	Total.
43·03	2·50	39·54	0·06	0·42	14·68	100·23
42·59	1·49	40·11	0·03	0·72	15·01	99·95
53·37	2·39	44·47	...	...	...	100·23
52·71	0·24	44·23	...	...	2·58	99·76
48·73	...	42·94	...	0·18	7·82	99·67

Dolomite

CaO.	MgO.	CO_2.	$Fe_2O_3+Al_2O_3$.	FeO.	H_2O.	Insoluble residue.	Total.
29·51	20·29	47·22	0·82	...	1·05	1·33	100·22
30·75	25·18	42·01	...	0·83	0·07	1·30	100·14
29·61	12·94	44·72	...	12·99	...	...	100·26

Portland Cement

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO	SO_3.	CO_2+H_2O.	Alkalis.	Insoluble residue.	Total.
21·88	6·26	3·20	63·92	1·17	1·42	1·40	0·43	2·22	99·90
24·40	4·76	2·43	64·70	1·20	1·30	0·56	0·64	0·15	100·14
21·76	6·77	3·43	62·56	1·14	1·25	1·72	0·69	0·75	100·07

Cassiterite

SnO_2.	Fe_2O_3.	CaO.	SiO_2.	Total.
98·74		0·41	0·19	99·46

Cassiterite often contains traces of As and Zn.

Garnet

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	H_2O.	Total.
40·92	22·45	5·46	8·11	0·46	17·85	5·04	0·10	100·39

Traces of Cr are usually found in garnets.

Manganese Minerals

	MnO_2.	MnO.	Fe_2O_3.	BaO.	H_2O.	Insoluble residue.	Total.
Pyrolusite . .	86·45	6·02	0·93	1·31	1·22	4·11	100·04
Pyrolusite . .	69·06	18·16	...	...	...	0·55	...
Manganite .	48·47	42·03	...	...	7·41	1·72	99·63

Zinc Blende

S.	Zn.	Cd.	Fe.	Mn.	Pb.	Total.
32·98	64·92	1·05	0·57	0·37	0·15	100·04
33·25	50·02	0·30	15·44	nil	1·01	100·02

Copper Pyrites

S.	Fe.	Cu.	Ag.	Pb.	Insoluble residue.	Total.
30·50	21·08	48·40	trace	...	...	99·98
33·18	32·65	32·79	nil	0·35	1·04	100·01
36·15	29·34	32·25	nil	0·30	2·09	100·13

Density and Concentration of Hydrochloric Acid at 15°

(*Normal* HCl = 36·47 *grams per litre*)

Density 15°/4°.	100 grams contain grams HCl.	1 litre contains grams HCl.	Normality.	Density 15°/4°.	100 grams contain grams HCl.	1 litre contains grams HCl.	Normality.
1·010	2·14	22	0·6	1·110	21·9	243	6·7
1·020	4·13	42	1·2	1·120	23·8	267	7·3
1·030	6·15	64	1·8	1·130	25·7	291	8·0
1·040	8·16	85	2·3	1·140	27·7	315	8·6
1·050	10·17	107	2·9	1·150	29·6	340	9·3
1·060	12·19	129	3·5	1·160	31·5	366	10·0
1·070	14·17	152	4·2	1·170	33·5	392	10·8
1·080	16·15	174	4·8	1·180	35·4	418	11·7
1·090	18·1	197	5·4	1·190	37·2	443	12·1
1·100	20·0	220	6·0	1·200	39·1	469	12·9

Density and Concentration of Sulphuric Acid at 15°

(*Normal* H_2SO_4 = 49·04 *grams per litre*)

Density 15°/4°.	100 grams contain grams H_2SO_4.	1 litre contains grams H_2SO_4.	Normality.	Density 15°/4°.	100 grams contain grams H_2SO_4.	1 litre contains grams H_2SO_4.	Normality.
1·006	1	10·1	0·20	1·449	55	797	16·25
1·013	2	20·3	0·41	1·502	60	901	18·38
1·020	3	30·4	0·62	1·558	65	1013	20·65
1·026	4	41·0	0·84	1·615	70	1130	23·05
1·033	5	51·6	1·05	1·674	75	1248	25·60
1·040	6	62·4	1·27	1·732	80	1386	28·26
1·047	7	73·3	1·49	1·784	85	1520	30·92
1·054	8	84·3	1·72	1·820	90	1640	33·40
1·061	9	95·5	1·95	1·825	91	1660	33·86
1·068	10	106·8	2·18	1·829	92	1680	34·32
1·104	15	160·6	3·38	1·833	93	1710	34·76
1·142	20	228	4·66	1·836	94	1730	35·20
1·182	25	296	6·02	1·839	95	1750	35·62
1·222	30	367	7·48	1·841	96	1770	36·03
1·264	35	444	9·02	1·841	97	1790	36·42
1·306	40	522	10·66	1·841	98	1800	36·79
1·351	45	608	12·40	1·839	99	1820	37·13
1·399	50	700	14·26	(1·836)	100	(1836)	(37·4)

Density and Concentration of Nitric Acid at 15°

(*Normal* HNO_3 = 63·02 *grams per litre*)

Density 15°/4°.	100 grams contain grams HNO_3.	1 litre contains grams HNO_3.	Normality.	Density 15°/4°.	100 grams contain grams HNO_3.	1 litre contains grams HNO_3.	Normality.
1·010	1·90	19	0·30	**1·280**	44·41	568	9·01
1·020	3·70	38	0·60	**1·300**	47·49	617	9·8
1·040	7·26	75	1·19	**1·320**	50·71	669	10·6
1·060	10·68	113	1·79	**1·340**	54·07	725	11·5
1·080	13·95	151	2·35	**1·360**	57·57	783	12·4
1·100	17·11	188	2·99	**1·380**	61·27	846	13·4
1·120	20·23	227	3·60	**1·400**	65·30	914	14·5
1·140	23·31	266	4·22	**1·420**	69·80	991	15·7
1·160	26·36	306	4·84	**1·440**	74·68	1075	17·1
1·180	29·38	347	5·51	**1·460**	79·98	1168	18·5
1·200	32·36	388	6·16	**1·480**	86·05	1274	20·2
1·220	35·28	430	6·83	**1·500**	94·1	1410	22·4
1·240	38·29	475	7·54	**1·510**	98·1	1480	23·5
1·260	41·34	521	8·25	**1·520**	99·7	1515	24·0

Density and Concentration of Perchloric Acid at 15°

Density 15°/4°.	100 grams contain grams $HClO_4$.	1 litre contains grams $HClO_4$.	Density. 15°/4°.	100 grams contain grams $HClO_4$.	1 litre contains grams $HClO_4$.
1·030	5·25	54	**1·240**	33·85	420
1·060	10·06	107	**1·270**	37·08	471
1·090	14·56	159	**1·300**	40·10	521
1·120	18·88	212	**1·360**	45·71	622
1·150	22·99	264	**1·420**	50·91	723
1·180	26·82	316	**1·540**	60·04	925
1·210	30·45	369	**1·675**	70·15	1175

Density and Concentration of Potassium Hydroxide at 15°

Density 15°/4°.	100 grams contain grams KOH.	1 litre contains grams KOH.
1·033	5	52
1·082	10	108
1·134	15	178
1·176	20	235
1·230	25	307
1·287	30	386
1·346	35	471
1·411	40	564
1·473	45	663
1·538	50	769

Density and Concentration of Sodium Hydroxide at 15°

Density 15°/4°.	100 grams contain grams NaOH.	1 litre contains grams NaOH.
1·058	5	53
1·113	10	111
1·170	15	175
1·224	20	245
1·279	25	320
1·332	30	400
1·383	35	484
1·433	40	573
1·481	45	666
1·529	50	765

Density and Concentration of Ammonia Solutions at 15°

(*Normal* NH_3 = 17·03 *grams per litre*)

Density 15°/4°.	100 grams contain grams NH_3.	1 litre contains grams NH_3.	Normality.	Density 15°/4°.	100 grams contain grams NH_3.	1 litre contains grams NH_3.	Normality.
0·990	2·31	22·9	1·3	0·930	18·64	173·4	10·2
0·980	4·80	47·0	2·8	0·920	21·75	210·1	11·8
0·970	7·31	70·9	4·2	0·910	24·99	227·4	13·4
0·960	9·91	95·1	5·6	0·900	28·33	255·0	15·0
0·950	12·74	121·0	7·1	0·890	31·75	282·6	16·6
0·940	15·63	146·9	8·6	0·880	35·70	314·2	18·5

Density of Aqueous Alcohol at 15°

Density 15°/4°.	Grams of alcohol per 100 grams.	Grams of alcohol per litre.	Density 15°/4°.	Grams of alcohol per 100 grams.	Grams of alcohol per litre.
0·983	10	98	0·872	70	610
0·971	20	194	0·860	75	645
0·957	30	287	0·848	80	678
0·939	40	376	0·835	85	710
0·918	50	459	0·822	90	740
0·895	60	537	0·808	95	768
0·884	65	574	0·793	100	793

Weight of 1 Litre of Various Dry Gases at 0° and 760 mm.

	Grams.		Grams.
Air	1·2928	Methane . . .	0·7170
Carbon monoxide . .	1·2506	Nitric oxide . . .	1·3402
Carbon dioxide . .	1·9770	Nitrogen . . .	1·2505
Hydrogen . . .	0·0900	Oxygen	1·4292

Vapour Pressure of Water

Temperature.	Vapour Pressure.	Temperature.	Vapour Pressure.	Temperature.	Vapour Pressure.
Degrees.	mm.	Degrees.	mm.	Degrees.	mm.
4	6·1	14	11·9	24	22·2
5	6·5	15	12·7	25	23·5
6	7·0	16	13·6	26	25·0
7	7·5	17	14·4	27	26·5
8	8·0	18	15·4	28	28·1
9	8·6	19	16·4	29	29·8
10	9·2	20	17·4	30	31·5
11	9·8	21	18·5	31	33·4
12	10·5	22	19·7	32	35·4
13	11·2	23	20·9	33	37·4

Vapour Pressure of Potassium Hydroxide Solutions

Temperature.	Vapour pressure of 40 per cent. solution.	Vapour pressure of 50 per cent. solution.
Degrees.	mm.	mm.
10	6·5	5·6
12	7·5	6·5
14	8·4	7·3
16	9·6	8·3
18	10·9	9·5
20	12·4	10·8
22	13·9	12·1

The "40 per cent." solution is one containing 40 grams of potassium hydroxide added to 100 grams of water, and the "50 per cent." solution one containing 50 grams of potassium hydroxide added to 100 grams of water.

Table to be used in determining the volume of glass apparatus by weighing the water contained in or delivered by it at a given temperature, when 15° C. is taken as the standard temperature for glass apparatus. (See p. 45.)

t° C.	Nominal capacity of vessel in millilitres.								
	5.	10.	20.	25.	50.	100.	250.	500.	1000.
10	0·007	0·015	0·030	0·037	0·074	0·148	0·370	0·74	1·48
11	0·008	0·015	0·031	0·039	0·077	0·155	0·385	0·77	1·55
12	0·008	0·016	0·033	0·041	0·081	0·163	0·405	0·81	1·63
13	0·009	0·017	0·034	0·043	0·086	0·172	0·430	0·86	1·72
14	0·009	0·018	0·037	0·046	0·091	0·183	0·455	0·91	1·83
15	0·010	0·019	0·039	0·049	0·097	0·195	0·485	0·97	1·95
16	0·010	0·021	0·042	0·052	0·104	0·208	0·520	1·04	2·08
17	0·011	0·022	0·044	0·056	0·111	0·222	0·555	1·11	2·22
18	0·012	0·024	0·047	0·059	0·119	0·237	0·595	1·19	2·37
19	0·013	0·025	0·051	0·063	0·127	0·254	0·635	1·27	2·54
20	0·014	0·027	0·054	0·068	0·136	0·271	0·680	1·36	2·71
21	0·014	0·029	0·058	0·072	0·145	0·290	0·725	1·45	2·90
22	0·015	0·031	0·062	0·077	0·155	0·309	0·775	1·55	3·09
23	0·017	0·033	0·066	0·083	0·165	0·330	0·825	1·65	3·30
24	0·018	0·035	0·070	0·088	0·176	0·352	0·880	1·76	3·52
25	0·018	0·037	0·074	0·093	0·187	0·374	0·935	1·87	3·74

Logarithms

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
100	0000	0004	0009	0013	0017	0022	0026	0030	0035	0039									
101	0043	0048	0052	0056	0060	0065	0069	0073	0077	0082									
102	0086	0090	0095	0099	0103	0107	0111	0116	0120	0124									
103	0128	0133	0137	0141	0145	0149	0154	0158	0162	0166									
104	0170	0175	0179	0183	0187	0191	0195	0199	0204	0208									
105	0212	0216	0220	0224	0228	0233	0237	0241	0245	0249									
106	0253	0257	0261	0265	0269	0273	0278	0282	0286	0290									
107	0294	0298	0302	0306	0310	0314	0318	0322	0326	0330									
108	0334	0338	0342	0346	0350	0354	0358	0362	0366	0370									
109	0374	0378	0382	0386	0390	0394	0398	0402	0406	0410									
110	0414	0418	0422	0426	0430	0434	0438	0441	0445	0449									
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

Logarithms

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

GENERAL REFERENCES

BOOKS

General Quantitative Analysis.

TREADWELL, F. P.—Analytical Chemistry. Vol. II. Translated and enlarged by W. T. Hall. London: Chapman & Hall, Ltd. A text-book for advanced students, giving a systematic account of the more important methods of determination and separation.

MELLOR, J. W.—A Treatise on Quantitative Inorganic Analysis. London: Charles Griffin & Co., Ltd. Deals more especially with the analysis of clays, silicates, and related minerals, and is replete with references.

SCOTT, W. W., and FURMAN, N. H.—Standard Methods of Chemical Analysis. London: Technical Press. A manual of analytical methods and general reference for advanced students and professional chemists.

SMITH, J. B.—Analytical Processes. London: E. Arnold.

MITCHELL, A. D., and WARD, A. M.—Modern Methods in Quantitative Chemical Analysis. London: Longmans, Green & Co.

MITCHELL, C. A. (Editor).—Recent Advances in Analytical Chemistry. Vol. II., Inorganic. London: J. & A. Churchill. Contains articles by a number of authorities.

KOLTHOFF and SANDELL.—Text-book of Quantitative Inorganic Analysis. Macmillan & Co.

Volumetric Analysis.

KOLTHOFF, I. M., and FURMAN, N. H.—Volumetric Analysis. Vol. I., Theoretical; Vol. II., Practical. London: Chapman & Hall, Ltd. A comprehensive exposition of the theoretical principles of volumetric analysis from the modern standpoint, and a detailed account of the application of these principles in laboratory practice.

BÖTTGER, W.—Newer Methods of Volumetric Chemical Analysis. Translated by Oesper, R. E. London: Chapman & Hall, Ltd.

SUTTON, F.—A Systematic Handbook of Volumetric Analysis. London: J. & A. Churchill. A standard book of reference.

KNECHT, E., and HIBBERT, E.—New Reduction Methods in Volumetric Analysis. London: Longmans, Green & Co. Mainly an account of methods based on the use of titanous chloride as a quantitative reducing agent.

Volumetric Analysis—*continued.*

FOWLES, G.—Volumetric Analysis. London: G. Bell & Sons, Ltd. This book includes a large amount of recent work.

Qualitative Analysis (Inorganic).

TREADWELL, F. P.—Analytical Chemistry. Vol. I. Translated and revised by W. T. Hall. London: Chapman & Hall, Ltd.

STIEGLITZ, J.—The Elements of Qualitative Analysis. 2 Vols. London: G. Bell & Sons, Ltd.

KAY, S. A.—Qualitative Analysis of Inorganic Substances. London: Gurney & Jackson.

NOYES, A. A., and BRAY, W. C.—A System of Qualitative Analysis for the Rare Elements. London: Macmillan & Co., Ltd.

FEIGL, F.—Qualitative Analysis by Spot Tests. Translated by Mathews, J. W. Amsterdam and New York: Nordemann Publishing Coy.

Electrochemical Methods.

CLASSEN, A.—Quantitative Analysis by Electrolysis. Translated by W. T. Hall. London: Chapman & Hall, Ltd.

GRANT, J.—The Measurement of Hydrogen Ion Concentration. London: Longmans, Green & Co., Ltd.

KOLTHOFF, I. M., and FURMAN, N. H.—Potentiometric Titrations. London: Chapman & Hall, Ltd.

BRITTON, H. T. S.—Conductometric Analysis. London: Chapman & Hall, Ltd.

SAND, H. J. S.—Electrochemistry and Electrochemical Analysis. Vols. I and II. London: Blackie & Sons, Ltd.

Rock Analysis.

HILLEBRAND, W. F.—The Analysis of Silicate and Carbonate Rocks. Bulletin 700, U.S. Geological Survey. Washington: Government Printing Office. The most comprehensive treatise on this special topic that has been published.

WASHINGTON, H. S.—Manual of the Chemical Analysis of Rocks. London: Chapman & Hall, Ltd. The practical details of manipulation are most minutely described in this manual, which, together with Hillebrand's book, ought to be in the hands of every student who wishes to perfect himself in this difficult branch of analysis.

LOW, A. H.—Technical Methods of Ore Analysis. London: Chapman & Hall, Ltd. A valuable collection of rapid methods.

Technical and Industrial Analysis.

LUNGE, G., and KEANE, C. A.—Technical Methods of Chemical Analysis. 3 Vols. London: Gurney & Jackson. The technical methods of analysis applicable in all the important inorganic and organic industries are dealt with in separate sections.

HILLEBRAND, W. F., and LUNDELL, G. E. F.—Applied Inorganic Analysis, with special reference to the analysis of Metals, Minerals, and Rocks. London: Chapman & Hall, Ltd.

BLAIR, A. A.—The Chemical Analysis of Iron. Philadelphia and London: J. B. Lippincott Company. Contains the best methods for the analysis of iron, steel, and related raw materials.

IBBOTSON, F., and AITCHISON, L.—The Analysis of Non-Ferrous Alloys. London: Longmans, Green & Co. Aims at presenting the methods which, as far as possible, combine accuracy with convenience and rapidity.

THRESH, J. C.—The Examination of Water and Water Supplies. London: J. & A. Churchill. This volume describes the chemical, bacteriological, biological, and microscopical examination of water for domestic and industrial uses.

UNITED STEEL COMPANIES, LTD., SHEFFIELD (Publishers).—Standard Methods of Analysis of Iron, Steel, and Ferro-Alloys. This describes the methods used throughout the Companies' laboratories.

Gas Analysis.

DENNIS, L. M.—Gas Analysis. London: Macmillan & Co., Ltd. Deals for the most part with rapid technical methods, but describes also certain methods of exact analysis with mercury as the confining liquid.

LUNGE, G.—Technical Gas-Analysis. London: Gurney & Jackson.

HALDANE, J. S., and GRAHAM, J.—Methods of Air Analysis. London: Charles Griffin & Co., Ltd.

Chemical and Physical Constants and Technological Data, etc.

LANDOLT-BÖRNSTEIN.—Physikalisch-Chemische Tabellen. Berlin: Julius Springer.

KAYE, G. W. C., and LABY, T. H.—Tables of Physical and Chemical Constants, and Some Mathematical Functions. London: Longmans, Green & Co.

LUNGE, G.—Technical Chemists' Handbook. London: Gurney & Jackson.

SEIDELL, A.—Solubilities of Inorganic and Organic Substances. London: Crosby Lockwood & Son.

Chemical and Physical Constants, etc.—*continued*

HODGMAN, C. E., and LANGE, N. A.—Handbook of Chemistry and Physics. Cleveland, Ohio, US.A. Chemical Rubber Publishing Co. A very comprehensive reference book of chemical and physical data.

WASHBURN, E. W.—International Critical Tables. London: McGraw-Hill.

JOURNALS AND PERIODICALS

The Analyst.—The Journal of the Society of Public Analysts and other Analytical Chemists. London: Simpkin, Marshall, Hamilton, Kent, & Co., Ltd. A Monthly Journal containing Papers read before the Society, and Abstracts of Papers on Analytical Chemistry published in other Journals.

Annual Reports of the Progress of Chemistry.—Issued by the Chemical Society. London: Gurney & Jackson. The Reports present an epitome of the principal advances that have been made in the preceding year. One of the Reports in each annual volume reviews the progress in Analytical Chemistry, with references to the Journals in which the original papers are to be found.

Journal of the Society of Chemical Industry.—A Monthly Journal containing a record of all important work and news connected with Chemical Industry, including Papers read before the Society, and Abstracts of the Literature of Applied Chemistry.

Industrial and Engineering Chemistry: Analytical Edition.—A Monthly Journal devoted to Analytical Chemistry published by the American Chemical Society.

Zeitschrift für Analytische Chemie.—A Journal issued at frequent intervals corresponding to *The Analyst.*

INDEX OF SEPARATIONS

GENERAL methods of separation are discussed briefly in the systematic section (p. 275) under the headings of the various elements.

The following index gives references to the separations that are more fully described.

INDEX

Atomic Weights

(Based on International Atomic Weights for 1940)

Element	Symbol	Atomic Weight
Aluminium	Al	26·97
Antimony	Sb	121·8
Argon	A	39·94
Arsenic	As	74·91
Barium	Ba	137·4
Beryllium	Be	9·02
Bismuth	Bi	209·0
Boron	B	10·82
Bromine	Br	79·92
Cadmium	Cd	112·4
Cæsium	Cs	132·9
Calcium	Ca	40·08
Carbon	C	12·01
Cerium	Ce	140·1
Chlorine	Cl	35·457
Chromium	Cr	52·01
Cobalt	Co	58·94
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·2
Europium	Eu	152·0
Fluorine	F	19·00
Gadolinium	Gd	156·9
Gallium	Ga	69·72
Germanium	Ge	72·60
Gold	Au	197·2
Hafnium	Hf	178·6
Helium	He	4·003
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·9
Iridium	Ir	193·1
Iron	Fe	55·85
Krypton	Kr	83·7
Lanthanum	La	138·9
Lead	Pb	207·2
Lithium	Li	6·94
Lutecium	Lu	175·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	95·95
Neodymium	Nd	144·3
Neon	Ne	20·18
Nickel	Ni	58·69
Niobium (Columbium)	Nb	92·91
Nitrogen	N	14·008
Osmium	Os	190·2
Oxygen	**O**	**16·000**
Palladium	Pd	106·7
Phosphorus	P	30·98
Platinum	Pt	195·2
Potassium	K	39·096
Praseodymium	Pr	140·9
Radium	Ra	226·0
Radon	Rn	222·0
Rhenium	Re	186·3
Rhodium	Rh	102·9
Rubidium	Rb	85·48
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	45·1
Selenium	Se	78·96
Silicon	Si	28·06
Silver	Ag	107·88
Sodium	Na	22·997
Strontium	Sr	87·63
Sulphur	S	32·06
Tantalum	Ta	180·9
Tellurium	Te	127·6
Terbium	Tb	159·2
Thallium	Tl	204·4
Thorium	Th	232·[illegible]
Thulium	Tm	169·4
Tin	Sn	118·7
Titanium	Ti	47·90
Tungsten	W	183·9
Uranium	U	238·1
Vanadium	V	50·95
Xenon	Xe	131·3
Ytterbium	Yb	173·0
Yttrium	Yt	88·92
Zinc	Zn	65·38
Zirconium	Zr	91·22